RECEIPT OF REGULATORY REQUESTED DOCUMENTS

TITLE: WASHINGTON STATE DEPARTMENT OF ECOLOGY REQUEST FOR COPY OF ARGONNE EAST CEMENTED DRUMS DESIGNATION INFORMATION PACKAGE DATED SEPTEMBER 22, 2011

CH2M HILL PRC REPRESENTATIVE: Joel F. Williams Jr

REGULATORY AGENCY: WASHINGTON STATE DEPARTMENT OF ECOLOGY

DOE/RL RREPRESENTATIVE: Mike Collins

Requested Information:

1. Copy of "Argonne East Cemented Drum Designation Information Package," dated September 22, 2011 (69 pages)

Central Files _____
File Name: _____
Cross Reference: _____

REPRESENTATIVE NAME AND TITLE:
(PRINT): Albert Chang/Ecology

SIGNATURE: _____ DATE: 12-12-2011

CHPRC REPRESENTATIVE NAME AND TITLE:
(PRINT): Joel F. Williams Jr.

SIGNATURE: _____ DATE: 12-12-2011

DON'T SAY IT — *Write It!*

TO: File T4-06

cc:

DATE: September 22, 2011

FROM: Mel Lakes T4-06

Telephone: 373-0043

SUBJECT: Argonne East Cemented Drums Designation Information Package

Background:

The Argonne-East waste consists of neutralized acid solution of dissolved fuel rods containing ^{233}U and ^{232}Th from the Argonne-East Proof of Breeder (POB) program. The acid solution was neutralized with slaked lime and mixed with cement. The cemented drums were received at Hanford from June 1985 through September 1985. The dissolver solution from Argonne-East was cemented and neutralized with slaked lime in 5.7-L (1.5-gal) cans.

Information:

The Acceptable Knowledge Summary Report of the Argonne National Laboratory Waste, WMP-32026 was completed in 2007. Attachment 1-A is the updated Argonne-East Cemented Drums designation (ANL-DES-01-01). Attachment 1-B is the original Argonne-East Cemented Drums designation (ANL-DES-01-00). Attachment 2 is a list of the 42 cemented containers along with the background information for updating the designation. Attachment 3 provides the conservative calculations for the chromium and cadmium. Attachment 4 contains the reference documents that were used to perform the calculations in Attachment 3. Attachment 5 is the hand calculation for Nickel which has the highest component weight percent (70%) in Inconel X-750 metal.

The updated designation has been developed due to new information provided in the attachments, designation ANL-DES-01-00, WMP-370, 2.34, and the WMP-370, 5.1 procedures. Revised calculations were performed with the addition of steel and cement as part of the waste matrix. The internal cement and metal container were added to the waste matrix. The original designation ANL-DES-01-00 did not account for the cement or inner container metal as part of the waste matrix. Designation ANL-DES-01-00 conservatively assigned the cadmium (D006), chromium (D007), and lead (D008) waste codes.

Designation ANL-DES-01-01 used the following information for cadmium, chromium and lead for the cemented drums:

- D006 waste code – Cadmium was calculated to be 1.4E-05 ppm which is below the regulatory limit of 1mg/l TCLP (1 ppm).
- D007 waste code – Chromium was calculated to be 1.0 ppm which is below the regulatory limit of 5 mg/l TCLP (5 ppm).
- D008 waste code - Lead is not part of the waste matrix and was clearly used as shielding. The D008 waste code will not apply for lead used as shielding.

Lime (10ppm), nitric acid (10ppm), and hydrofluoric acid (10ppm) were identified in the designation at very low amounts. The liquid solution waste solidified with cement. Nickel was one of the highest component amounts in the metal composition and was added to the designation.

Conclusion:

Based on the information provided and the calculations the D006, D007, and D008 waste codes will not apply to the cemented drums from Argonne East. The waste was designation as low level waste.

Attachments:

- Attachment 1- Argonne National Laboratory Designations
  - 1-A, Updated Argonne-East Cemented Drums designation (ANL-DES-01-01)
  - 1-B, Original Argonne-East Cemented Drums designation (ANL-DES-01-00).
- Attachment 2, List of the 42 cemented containers along with the background information for updating the designation.
- Attachment 3, Calculations for the chromium and cadmium.
- Attachment 4, Reference documents for calculations in Attachment 3.
- Attachment 5, Calculation for Nickel (the highest component weight percent, i.e., 70%, in Inconel X-750 metal.

ATTACHMENT 1A

Sum of Weight%: 105.0035020

Characteristic WAC-173-303-090-5-7

Flashpoint < 60C IGNITABLE	D001 DW	NA
* OXIDIZER	D001 DW	NA
pH <=2 or >= 12.5 (Liquids)	D002 DW	NA
(Solids Only)	WSC2 DW	NA
Reactive	D003 DW	NA

*Oxidizer defined in 49CFR 173.127 & 173.128

Toxic Dangerous Waste WAC 173-303-100

Total EC %: .0001100 -

No data or EC% < .001	Non-Reg	✓
EC% >=.001 & <1	WT02 DW	NA
EC% >= 1	WT01 EHW	NA

Persistent Dangerous Waste WAC-173-303-100

Total HOC%: .0000000 Total PAH%: .0000000

No HOC/PAH or below limits	Non-Reg	✓
HOC% > 1	WP01 EHW	NA
HOC% 0.01 to 1	WP02 DW	NA
PAH% > 1%	WP03 EHW	NA

Toxicity Characteristic WAC 173-303-090-8

TC CODES NONE

MATERIAL USED AS SOLVENTS: NONE

APPLICABLE WASTE CODES: NONE

APPLICABLE LDR CODES: NONE WASTE CLASS: NA

COMMENTS: NON-Regulated Waste

Designation Specialist: MEL LAKES (Print Name) Mel Lakes (Signature) 9-9-11 (Date)

For Designation # ANL-DES-01-01

Description: REDESIGNATION FOR THE CEMENTED URANIUM-233 AND THORIUM-232 FROM ARGONNE RESEARCH FOR THE NAVY'S PROOF-OF-BREEDING REACTOR PROGRAMS. DESIGNATION BASED ON WMP-370, 2.34 AND 5.1 FOR IDENTIFING COMPONENTS IN THE DESIGNATION.

Entry Date: 08/26/11 **Physical State:** Solid **pH:** >2 - <12.5 **Flashpoint:** NA C

Designator: ME LAKES **Old/Spill/Used:** Used

Comments: ADDITIONAL INFORMATION PROVIDED FOR THE CONTAINERS. THE CONCRETE IS IDENTIFIED AS WASTE. ALL CHARACTERISTIC ARE BELOW REGULATORY AMOUNTS. LEAD WAS REMOVED AS WASTE (NO EVIDENCE LEAD IS IN THE WASTE). CHROMIUM IS BELOW REGULATORY LIMITS. ACIDS WERE NEUTRALIZED AND CONCRETED INPUTTED AT 10 PPM. LIME INPUTTED AT 10 PPM. IMPURITIES NOT ADDED TO DESIGNATION.

CAS#	Chemical Name	IGNT	REAC	CORR	PERS	UHC	WW Limit	NWW Limit	Listed/TC Codes(limit mg/l)
1332-69-0	LIME	NA	N	NA	NA	N			

Source	ID#	Weight %	EC %	TOX: N
VC	1332-69-0	.0010000	.0000000	
Totals per CAS #:		.0010000	.0000000	

CAS#	Chemical Name	IGNT	REAC	CORR	PERS	UHC	WW Limit	NWW Limit	Listed/TC Codes(limit mg/l)
2439-89-6	STEEL (IRON)	NA	N	NA	NA	N			

Source	ID#	Weight %	EC %	TOX: N
IC	2439-89-6	31.0000000	.0000000	
Totals per CAS #:		31.0000000	.0000000	

CAS#	Chemical Name	IGNT	REAC	CORR	PERS	UHC	WW Limit	NWW Limit	Listed/TC Codes(limit mg/l)
65997-15-1	PORTLAND CEMENT	NA	N	B	NA	N			WSC2

Source	ID#	Weight %	EC %	TOX: N
IC	65997-15-1	74.0000000	.0000000	
Totals per CAS #:		74.0000000	.0000000	

CAS#	Chemical Name	IGNT	REAC	CORR	PERS	UHC	WW Limit	NWW Limit	Listed/TC Codes(limit mg/l)
7440-02-0	NICKEL	NA	N	NA	NA	X 5	3.98 mg/l	11 mg/l TCLP	

Source	ID#	Weight %	EC %	TOX: N
C	7440-02-0	.0004020	.0000000	
Totals per CAS #:		.0004020	.0000000	

CAS#	Chemical Name	IGNT	REAC	CORR	PERS	UHC	WW Limit	NWW Limit	Listed/TC Codes(limit mg/l)
7440-43-9	CADMIUM	NA	N	NA	NA	~~X~~ 5;	.69 mg/l	.11 mg/l TCLP	D~~0~~06 (1.0000); WT~~0~~1 3d 3d

Source	ID#	Weight %	EC %	TOX: A
WC	7440-43-9	.0000000	.0000000	
Totals per CAS #:		.0000000	.0000000	

CAS#	Chemical Name	IGNT	REAC	CORR	PERS	UHC	WW Limit	NWW Limit	Listed/TC Codes(limit mg/l)
7440-47-3	CHROMIUM	NA	N	NA	NA	~~X~~ 5;	2.77 mg/l	.6 mg/l TCLP	D~~0~~07 (5.0000) 3d

Source	ID#	Weight %	EC %	TOX: N
WC	7440-47-3	.0001000	.0000000	
Totals per CAS #:		.0001000	.0000000	

CAS#	Chemical Name	IGNT	REAC	CORR	PERS	UHC	WW Limit	NWW Limit	Listed/TC Codes(limit mg/l)
7664-39-3	HYDROFLUORIC ACID	NA	N	~~X~~ 3d,e	NA	N			D~~0~~02; U~~1~~34; WT~~0~~1 3d,e 1 3d

Source	ID#	Weight %	EC %	TOX: B
WC	7664-39-3	.0010000	.0000100	
Totals per CAS #:		.0010000	.0000100	

CAS#	Chemical Name	IGNT	REAC	CORR	PERS	UHC	WW Limit	NWW Limit	Listed/TC Codes(limit mg/l)
7697-37-2	NITRIC ACID	~~0~~ 3d,e	N	~~X~~ 3d,e	NA	N			D~~0~~01; D~~0~~02; WT~~0~~1 3d,e 3d,e 3d

Source	ID#	Weight %	EC %	TOX: A
WC	7697-37-2	.0010000	.0001000	
Totals per CAS #:		.0010000	.0001000	

Designation # ANL-DES-01-01 M 9/9/11

Designation Codes

(1) **Not a discarded chemical product (old/unused or sole active ingredient) (WAC 173-303-9903)** -

(2) **Not a dangerous waste source (used/spent) (WAC 173-303-9904)**

(3) **Does not exhibit dangerous waste characteristic / criteria per:**
- a) MSDS
- b) Lab analysis
- c) Generator knowledge
- d) Insufficient concentration M 9-9-11
- e) Not in this waste form M 9-9-11

(4) **Federal listed waste code takes precedence (40 CFR 268.9)**

(5) **Underlying Hazardous Constituent(s) not applicable per:**
- a) Alternative treatment standard – hazardous debris (40 CFR 268.45)
- b) Transuranic waste
- c) Federal waste code assigned that does not specify meeting 40 CFR 268.48 universal treatment standards
- d) Federal listed waste code assigned
- e) Federal characteristic waste code assigned
- f) Federal characteristic waste code not assigned
- g) Insufficient concentration (40 CFR 268.48)
- h) Not an UHC in characteristic wastes, according to the definition at 40 CFR 268.2(i)
- i) No waste code assigned that specifies meeting 40 CFR 268.48 universal treatment standards M 9-9-11
- j) To be determined based on treatment/disposal path

(6) ****Exclude:**
- a) WT01 EHW Washington State waste code, because Federal listed and/or characteristic waste code(s) assigned. Additional designation not required in accordance with WAC 173-303-070(5)
- b) WT02 DW Washington State waste code, because Federal listed and/or characteristic waste code(s) assigned. Additional designation not required in accordance with WAC 173-303-070(5)
- c) WP01 EHW Washington State waste code, because Federal listed and/or characteristic waste code(s) assigned. Additional designation not required in accordance with WAC 173-303-070(5)
- d) WP02 DW Washington State waste code, because Federal listed and/or characteristic waste code(s) assigned. Additional designation not required in accordance with WAC 173-303-070(5)
- e) WP03 EHW Washington State waste code, because Federal listed and/or characteristic waste code(s) assigned. Additional designation not required in accordance with WAC 173-303-070(5)
- f) Exclude Washington State waste code, waste regulated under CERCLA and/or TSCA, not RCRA or WAC 173-303

ATTACHMENT 1B

H0073121 WASTE DESIGNATION WORKSHEET SWIR601

For Designation # ANL-DES-01-00

Sum of Weight%: 105.1791000

Characteristic WAC-173-303-090-5-7

Flashpoint < 60C IGNITABLE D001 DW ____

* OXIDIZER D001 DW ____

pH <=2 or >= 12.5 (Liquids) D002 DW ____

(Solids Only) WSC2 DW ____

Reactive D003 DW ____

*Oxidizer defined in 49CFR 173.127 & 173.128

Toxic Dangerous Waste WAC 173-303-100

Total EC %: .0016761

No data or EC% < .001 Non-Reg ____

EC% >=.001 & <1 WT02 DW ____

EC% >= 1 WT01 EHW ____

Persistent Dangerous Waste WAC-173-303-100

Total HOC%: .0000000 Total PAH%: .0000000

No EOC/PAH or below limits Non-Reg ____

HOC% > 1 WP01 EHW ____

HOC% 0.01 to 1 WP02 DW ____

PAH% > 1% WP03 EHW ____

Toxicity Characteristic WAC 173-303-090-8

TC CODES D006, D007, D008

MATERIAL USED AS SOLVENTS: None

APPLICABLE WASTE CODES: D006, D007, D008

APPLICABLE LDR CODES: To be determined at final disposal. WASTE CLASS: DW

COMMENTS:

Designation Specialist: Julie Waddoups (Print Name) Julie Waddoups (Signature) 1-10-07 (Date)

12/21/2006 01:15:18 PM

For Designation # ANL-DES-01-00

Description: CEMENTED URANIUM-233 AND THORIUM-232 FROM ARGONNE RESEARCH FOR THE NAVY'S PROOF-OF-BREEDING REACTOR PROGRAMS.

Entry Date: 11/28/06 Physical State: Solid pH: Flashpoint: C

Designator: JM WADDOUPS Old/Spill/Used: Used

Comments:

CAS#	Chemical Name	IGNT	REAC	CORR	PERS	UHC	WW Limit	NWW Limit	Listed/TC Codes (limit mg/l)
1332-69-0	LIME	NA	N	NA	NA	N			

Source	ID#	Weight %	EC %	TOX: N
WC	1332-69-0	.0100000	.0000000	
Totals per CAS #:		.0100000	.0000000	

CAS#	Chemical Name	IGNT	REAC	CORR	PERS	UHC	WW Limit	NWW Limit	Listed/TC Codes (limit mg/l)
2439-89-6	STEEL (IRON)	NA	N	NA	NA	N			

Source	ID#	Weight %	EC %	TOX: N
WC	2439-89-6	31.0000000	.0000000	
Totals per CAS #:		31.0000000	.0000000	

CAS#	Chemical Name	IGNT	REAC	CORR	PERS	UHC	WW Limit	NWW Limit	Listed/TC Codes (limit mg/l)
65996-67-0	IRON	NA	N	NA	NA	N			

Source	ID#	Weight %	EC %	TOX: N
WC	65996-67-0	.0100000	.0000000	
Totals per CAS #:		.0100000	.0000000	

CAS#	Chemical Name	IGNT	REAC	CORR	PERS	UHC	WW Limit	NWW Limit	Listed/TC Codes (limit mg/l)
65997-15-1	PORTLAND CEMENT	NA	N	~~P~~ 3e 5e	NA	N		3e 5e	~~WSCE~~

Source	ID#	Weight %	EC %	TOX: N
WC	65997-15-1	74.0000000	.0000000	
Totals per CAS #:		74.0000000	.0000000	

CAS#	Chemical Name	IGNT	REAC	CORR	PERS	UHC	WW Limit	NWW Limit	Listed/TC Codes (limit mg/l)
7429-90-5	ALUMINUM	~~FS~~	~~Y~~	NA	NA	N			~~D001; D003~~
		3d,3e	3d,3e	Compatibility				Reactivity	3d,e 3d,e
								~~WATER REACTIVE~~	
								3d,3e	

Source	ID#	Weight %	EC %	TOX: N
WC	7429-90-5	.0075000	.0000000	
Totals per CAS #:		.0075000	.0000000	

CAS#	Chemical Name	IGNT	REAC	CORR	PERS	UHC	WW Limit	NWW Limit	Listed/TC Codes (limit mg/l)
7439-92-1	LEAD	NA	N	NA	NA	~~Y~~ 5j	.69 mg/l	.75 mg/l TCLP	D008 (5.0000)

Source	ID#	Weight %	EC %	TOX: N
WC	7439-92-1	.0005000	.0000000	
Totals per CAS #:		.0005000	.0000000	

CAS#	Chemical Name	IGNT	REAC	CORR	PERS	UHC	WW Limit	NWW Limit	Listed/TC Codes (limit mg/l)
7439-95-4	MAGNESIUM	~~FS~~	~~Y~~	NA	NA	N			~~D001; D003~~
		3d,e	3d,e	Compatibility				Reactivity	3d,e 3d,e
								~~WATER REACTIVE~~	
								3d,e	

Source	ID#	Weight %	EC %	TOX: N
WC	7439-95-4	.0015000	.0000000	
Totals per CAS #:		.0015000	.0000000	

CAS#	Chemical Name	IGNT	REAC	CORR	PERS	UHC	WW Limit	NWW Limit	Listed/TC Codes (limit mg/l)
7439-96-5	MANGANESE	~~FS~~	N	NA	NA	N			~~D001~~
		3d,e							3d,e

Source	ID#	Weight %	EC %	TOX: N
WC	7439-96-5	.0050000	.0000000	
Totals per CAS #:		.0050000	.0000000	

CAS#	Chemical Name	IGNT	REAC	CORR	PERS	UHC	WW Limit	NWW Limit	Listed/TC Codes (limit mg/l)
7439-98-7	MOLYBDENUM	NA	N	NA	NA	N			

Source	ID#	Weight %	EC %	TOX: N
WC	7439-98-7	.0050000	.0000000	
Totals per CAS #:		.0050000	.0000000	

CAS#	Chemical Name	IGNT	REAC	CORR	PERS	UHC	WW Limit	NWW Limit	Listed/TC Codes (limit mg/l)
7440-02-0	NICKEL	NA	N	NA	NA	X 5j	3.98 mg/l	11 mg/l TCLP	

Source	ID#	Weight %	EC %	TOX: N
WC	7440-02-0	.0070000	.0000000	
Totals per CAS #:		.0070000	.0000000	

CAS#	Chemical Name	IGNT	REAC	CORR	PERS	UHC	WW Limit	NWW Limit	Listed/TC Codes (limit mg/l)
7440-03-1	NIOBIUM	NA	N	NA	NA	N			

Source	ID#	Weight %	EC %	TOX: N
WC	7440-03-1	.0100000	.0000000	
Totals per CAS #:		.0100000	.0000000	

CAS#	Chemical Name	IGNT	REAC	CORR	PERS	UHC	WW Limit	NWW Limit	Listed/TC Codes (limit mg/l)
7440-19-9	SAMARIUM	NA	N	NA	NA	N			

Source	ID#	Weight %	EC %	TOX: N
WC	7440-19-9	.0010000	.0000000	
Totals per CAS #:		.0010000	.0000000	

CAS#	Chemical Name	IGNT	REAC	CORR	PERS	UHC	WW Limit	NWW Limit	Listed/TC Codes (limit mg/l)
7440-21-3	SILICON	~~PS~~ 3d,e	N	NA	NA	N			~~b001~~ 3d,e

Source	ID#	Weight %	EC %	TOX: D
WC	7440-21-3	.0100000	.0000010	
Totals per CAS #:		.0100000	.0000010	

CAS#	Chemical Name	IGNT	REAC	CORR	PERS	UHC	WW Limit	NWW Limit	Listed/TC Codes (limit mg/l)
7440-25-7	TANTALUM	NA	N	NA	NA	N			

Source	ID#	Weight %	EC %	TOX: N
WC	7440-25-7	.0100000	.0000000	
Totals per CAS #:		.0100000	.0000000	

CAS#	Chemical Name	IGNT	REAC	CORR	PERS	UHC	WW Limit	NWW Limit	Listed/TC Codes (limit mg/l)
7440-29-1	THORIUM	NA	N	NA	NA	N			

Source	ID#	Weight %	EC %	TOX: N
WC	7440-29-1	.0007000	.0000000	
Totals per CAS #:		.0007000	.0000000	

CAS#	Chemical Name	IGNT	REAC	CORR	PERS	UHC	WW Limit	NWW Limit	Listed/TC Codes (limit mg/l)
7440-31-5	TIN	NA	N	NA	NA	N			

Source	ID#	Weight %	EC %	TOX: N
WC	7440-31-5	.0100000	.0000000	
Totals per CAS #:		.0100000	.0000000	

CAS#	Chemical Name	IGNT	REAC	CORR	PERS	UHC	WW Limit	NWW Limit	Listed/TC Codes (limit mg/l)
7440-32-6	TITANIUM	~~PS~~ 3d,e	N	NA	NA	N			~~D001~~ 3d,e

Source	ID#	Weight %	EC %	TOX: N
WC	7440-32-6	.0040000	.0000000	
Totals per CAS #:		.0040000	.0000000	

CAS#	Chemical Name	IGNT	REAC	CORR	PERS	UHC	WW Limit	NWW Limit	Listed/TC Codes (limit mg/l)
7440-33-7	TUNGSTEN	~~PS~~ 3d,e	N	NA	NA	N			~~D001~~ 3d,e

Source	ID#	Weight %	EC %	TOX: N
WC	7440-33-7	.0080000	.0000000	
Totals per CAS #:		.0080000	.0000000	

CAS#	Chemical Name	IGNT	REAC	CORR	PERS	UHC	WW Limit	NWW Limit	Listed/TC Codes (limit mg/l)
7440-42-8	BORON	~~P8~~ 3d,e	N	NA	NA	N			~~D001~~ 3d,e

Source	ID#	Weight %	EC %	TOX: D
WC	7440-42-8	.0005000	.0000001	
Totals per CAS #:		.0005000	.0000001	

CAS#	Chemical Name	IGNT	REAC	CORR	PERS	UHC	WW Limit	NWW Limit	Listed/TC Codes (limit mg/l)
7440-43-9	CADMIUM	NA	N	NA	NA	~~X~~ 5.j	.69 mg/l	.11 mg/l TCLP	D006 (1.0000); ~~WT01~~ 6a

Source	ID#	Weight %	EC %	TOX: A
WC	7440-43-9	.0001000	.0000100	
Totals per CAS #:		.0001000	.0000100	

CAS#	Chemical Name	IGNT	REAC	CORR	PERS	UHC	WW Limit	NWW Limit	Listed/TC Codes (limit mg/l)
7440-44-0	CARBON	NA	N	NA	NA	N			

Source	ID#	Weight %	EC %	TOX: N
WC	7440-44-0	.0100000	.0000000	
Totals per CAS #:		.0100000	.0000000	

CAS#	Chemical Name	IGNT	REAC	CORR	PERS	UHC	WW Limit	NWW Limit	Listed/TC Codes (limit mg/l)
7440-47-3	CHROMIUM	NA	N	NA	NA	~~X~~ 5.j	2.77 mg/l	.6 mg/l TCLP	D007 (5.0000)

Source	ID#	Weight %	EC %	TOX: N
WC	7440-47-3	.0005000	.0000000	
Totals per CAS #:		.0005000	.0000000	

CAS#	Chemical Name	IGNT	REAC	CORR	PERS	UHC	WW Limit	NWW Limit	Listed/TC Codes (limit mg/l)
7440-48-4	COBALT	NA	N	NA	NA	N			

Source	ID#	Weight %	EC %	TOX: N
WC	7440-48-4	.0020000	.0000000	
Totals per CAS #:		.0020000	.0000000	

CAS#	Chemical Name	IGNT	REAC	CORR	PERS	UHC	WW Limit	NWW Limit	Listed/TC Codes (limit mg/l)
7440-50-8	COPPER	NA	N	NA	NA	N			

Source	ID#	Weight %	EC %	TOX: N
WC	7440-50-8	.0050000	.0000000	
Totals per CAS #:		.0050000	.0000000	

CAS#	Chemical Name	IGNT	REAC	CORR	PERS	UHC	WW Limit	NWW Limit	Listed/TC Codes (limit mg/l)
7440-54-2	GADOLINIUM	NA	N	NA	NA	N			

Source	ID#	Weight %	EC %	TOX: N
WC	7440-54-2	.0005000	.0000000	
Totals per CAS #:		.0005000	.0000000	

CAS#	Chemical Name	IGNT	REAC	CORR	PERS	UHC	WW Limit	NWW Limit	Listed/TC Codes (limit mg/l)
7440-58-6	HAFNIUM	~~P5~~ 3d,e	~~X~~ 3d,e	NA	NA	N		Reactivity 3d,e ~~PYROPHORIC~~ 3d,e	~~D001~~; ~~D003~~ 3d,e 3d,e

Source	ID#	Weight %	EC %	TOX: N
WC	7440-58-6	.0035000	.0000000	
Totals per CAS #:		.0035000	.0000000	

CAS#	Chemical Name	IGNT	REAC	CORR	PERS	UHC	WW Limit	NWW Limit	Listed/TC Codes (limit mg/l)
7440-61-1	URANIUM	~~P5~~ 3d,e	~~X~~ 3d,e	NA	NA	N		Reactivity 3d,e ~~PYROPHORIC~~ 3d,e	~~D001~~; ~~D003~~ 3d,e 3d,e

Source	ID#	Weight %	EC %	TOX: N
WC	7440-61-1	.0003000	.0000000	
Totals per CAS #:		.0003000	.0000000	

CAS#	Chemical Name	IGNT	REAC	CORR	PERS	UHC	WW Limit	NWW Limit	Listed/TC Codes (limit mg/l)
7440-62-2	VANADIUM	NA	N	NA	NA	X 5j	4.3 mg/l	1.6 mg/l TCLP	

Source	ID#	Weight %	EC %	TOX: N
WC	7440-62-2	.0050000	.0000000	
Totals per CAS #:		.0050000	.0000000	

CAS#	Chemical Name	IGNT	REAC	CORR	PERS	UHC	WW Limit	NWW Limit	Listed/TC Codes (limit mg/l)
7440-66-6	ZINC	~~FS~~ 3d,e	~~X~~ 3d,e	NA Compatibility	NA	~~X~~ 5j	2.61 mg/l	4.3 mg/l TCLP Reactivity PYROPHORIC, WATER REACTIVE 3d,e 3d,e	~~D001~~; ~~D003~~ 3d,e 3d,e

Source	ID#	Weight %	EC %	TOX: N
WC	7440-66-6	.0100000	.0000000	
Totals per CAS #:		.0100000	.0000000	

CAS#	Chemical Name	IGNT	REAC	CORR	PERS	UHC	WW Limit	NWW Limit	Listed/TC Codes (limit mg/l)
7440-67-7	ZIRCONIUM	~~FS~~ 3d,e	N	NA	NA	N			~~D001~~ 3d,e

Source	ID#	Weight %	EC %	TOX: N
WC	7440-67-7	.0100000	.0000000	
Totals per CAS #:		.0100000	.0000000	

CAS#	Chemical Name	IGNT	REAC	CORR	PERS	UHC	WW Limit	NWW Limit	Listed/TC Codes (limit mg/l)
7664-39-3	HYDROFLUORIC ACID	NA	N	~~A~~ 3d,e	NA	N			~~D002~~; ~~U134~~; ~~WT01~~ 3d,e 1 6a

Source	ID#	Weight %	EC %	TOX: B
WC	7664-39-3	.0100000	.0001000	
Totals per CAS #:		.0100000	.0001000	

CAS#	Chemical Name	IGNT	REAC	CORR	PERS	UHC	WW Limit	NWW Limit	Listed/TC Codes (limit mg/l)
7697-37-2	NITRIC ACID	~~O~~ 3d,e	N	A	NA	N			~~D001~~; ~~D002~~; ~~WT01~~ 3d,e 3d,e 6a

Source	ID#	Weight %	EC %	TOX: A
WC	7697-37-2	.0100000	.0010000	
Totals per CAS #:		.0100000	.0010000	

CAS#	Chemical Name	IGNT	REAC	CORR	PERS	UHC	WW Limit	NWW Limit	Listed/TC Codes (limit mg/l)
7723-14-0	PHOSPHORUS (RED, WHITE/YELLOW, BLACK/VIOLET)	~~ES~~ 3d,e	~~Y~~ 3d,e	NA	NA	N			~~D001; D003; WT02~~ 3d,e 3d,e 6b

Compatibility

Reactivity

~~OTHER~~ 3d,e

Source	ID#	Weight %	EC %	TOX: A
WC	7723-14-0	.0050000	.0005000	
Totals per CAS #:		.0050000	.0005000	

CAS#	Chemical Name	IGNT	REAC	CORR	PERS	UHC	WW Limit	NWW Limit	Listed/TC Codes (limit mg/l)
7782-41-4	FLUORINE	~~S~~ 3d,e	N	NA	NA	N			~~D001; P056; WT01~~ 3d,e 1 6a

Source	ID#	Weight %	EC %	TOX: B
WC	7782-41-4	.0050000	.0000500	
Totals per CAS #:		.0050000	.0000500	

CAS#	Chemical Name	IGNT	REAC	CORR	PERS	UHC	WW Limit	NWW Limit	Listed/TC Codes (limit mg/l)
7782-50-5	CHLORINE	NA	N	NA	NA	N			

Source	ID#	Weight %	EC %	TOX: B
WC	7782-50-5	.0015000	.0000150	
Totals per CAS #:		.0015000	.0000150	

A1.0 ARGONNE WASTE DESIGNATIONS

Designation # ANL-DES-01-00, ANL-DES-02-00, ANL-DES-03-00 WMP-32026 Rev. 0

Designation Codes

JW 1-10-07 (1) Not a discarded chemical product (old/unused or sole active ingredient) (WAC 173-303-9903)

JW 1-10-07 (2) Not a dangerous waste source (used/spent) (WAC 173-303-9904)

(3) Does not exhibit dangerous waste characteristic / criteria per:

a) MSDS

b) Lab analysis

JW 1-10-07 c) Generator knowledge

JW 1-10-07 d) Insufficient concentration

JW 1-10-07 e) Not in this waste form

(4) Federal listed waste code takes precedence (40 CFR 268.9)

(5) Underlying Hazardous Constituent(s) not applicable per:

a) Alternative treatment standard - hazardous debris (40 CFR 268.45)

b) Transuranic waste

c) Federal waste code assigned that does not specify meeting 40 CFR 268.48 universal treatment standards

d) Federal listed waste code assigned

JW 1-10-07 e) Federal characteristic waste code assigned

f) Federal characteristic waste code not assigned

g) Insufficient concentration (40 CFR 268.48)

h) Not an UHC in characteristic wastes, according to the definition at 40 CFR 268.2(i)

i) No waste code assigned that specifies meeting 40 CFR 268.48 universal treatment standards

JW 1-10-07 j) To be determined based on treatment/disposal path

(6) **Exclude:

JW 1-10-07 a) WT01 EHW Washington State waste code, because Federal listed and/or characteristic waste code(s) assigned. Additional designation not required in accordance with WAC 173-303-070(5)

JW 1-10-07 b) WT02 DW Washington State waste code, because Federal listed and/or characteristic waste code(s) assigned. Additional designation not required in accordance with WAC 173-303-070(5)

JW 1-10-07 c) WP01 EHW Washington State waste code, because Federal listed and/or characteristic waste code(s) assigned. Additional designation not required in accordance with WAC 173-303-070(5)

d) WP02 DW Washington State waste code, because Federal listed and/or characteristic waste code(s) assigned. Additional designation not required in accordance with WAC 173-303-070(5)

e) WP03 EHW Washington State waste code, because Federal listed and/or characteristic waste code(s) assigned. Additional designation not required in accordance with WAC 173-303-070(5)

f) Exclude Washington State waste code, waste regulated under CERCLA and/or TSCA, not RCRA or WAC 173-303

A-1

ATTACHMENT 2

Lakes, Melvin E (Mel)

From: Austin, Richard L
Sent: Tuesday, August 16, 2011 10:41 AM
To: Lakes, Melvin E (Mel)
Subject: FW: ANL-E Drum Summary - August 2011

Richard L. Austin
Materials & Energy Corporation
Technical Services - Team Lead Waste Acceptance
509-372-0678

From: Cornelison, Chad
Sent: Friday, August 12, 2011 2:38 PM
To: Nester, Dean E; Catlow, Rene L
Cc: Ware, Nancy W; Karschnia, Paul T; Miskho, Anthony G; Austin, Richard L
Subject: ANL-E Drum Summary - August 2011

The 42 ANL-E drums are currently stored in CWC as CH-MLLW (41 55-gal drums and 1 85-gal overpack with 55-gal inside). They should be considered RH-MLLW (Treatability Group MLLW-07) for any intrusive waste management activities or waste tracking. PINs include:

0038229	5208025	5208045	5208063
5208011	5208026	5208046	5208064
5208012	5208031	5208051	5208065
5208013	5208032	5208052	5208066
5208014	5208033	5208053	5208071
5208015	5208035	5208054	5208072
5208016	5208036	5208055	5208073
5208021	5208041	5208056	5208074
5208022	5208042	5208061	5208075
5208023	5208043	5208062	5208076
5208024	5208044		

The LLW Determination paper has good background information regarding this waste and justifies the 435.1 classification as MLLW (not SNF or HLW). Final DOE-RL comments and approvals received 8/10/11. Formal public release through document control was completed 8/11/11.

The following AK document was completed for the ANL-E waste in 2007: *Acceptable Knowledge Summary Report for the Argonne National Laboratory Waste* (WMP-32026), and is available in IDMS. Per the AK, the waste designated as MLLW for D006, D007, and D008 characteristic metal codes set at the regulatory limit (worst case designation). Conservative calculations performed by ANL-E and ourselves support the designation for D007, but not D006 or D008. It was determined since the D007 applied there was no real benefit to remove the D006 and D008 waste codes, so they were left on.

It was agreed upon that the best defensible disposition pathway for the waste was obtaining a site-specific treatment variance from Ecology and treating by in-cell MACRO at MWDUs. As time and priorities permitted, a treatment variance was submitted to DOE-RL for approval, and they submitted the treatment variance to Ecology on 5/16/11. The treatment variance was based on characterization of the inner containers holding cemented dissolver solution from test reactor research. The packaging and shielding components were not included in the calculations. Ecology suggested we

look at adding packaging in the waste weight and re-evaluate the regulatory status of the waste. There is some precedence for managing all container contents as waste, especially if the retrieval is considered the point of generation. This was brought up in a meeting with CHPRC/DOE-RL personnel on 8/9/11 and it was determined best not to include lead shielding in the evaluation, since the lead in these waste packages is clearly for shielding.

Revised calculations were performed using the previous methodology but with the addition of the steel/concrete components. The D007 result was less than the regulatory limit and would not designate as D007. Waste Support Services will work on getting addendums to the PIN files and redesignation as LLW (remove D006, D007, and D008 waste codes). When this is completed the waste will not require RCRA treatment for disposal in the MWDUs. The waste will still be WC3 LLW and require radiological stabilization (i.e., grouting).

> Actionees: Chad Cornelison and Rick Austin – Chad provided justification and revised calculations to Rick to complete Addendums. Waste Services will determine who is going to do the addendums. Target Sept 15th.

PINs 0038229 and 5208052 were non-destructively examined in the box vault at WRAP and the Waste Support Services determined they do not meet 90% full requirement for land disposal and that the package arrangement is not suitable for simple void filling like conducted for HTGR drums. A video tape of the NDE at WRAP is available for viewing. To date, waste packages not meeting 90% full have not been accepted for disposal in MWDUs (e.g., direct disposal, monoliths, or HICs). The ECOs and Waste Support Services will need to resolve this issue before they can be disposed in a monolith or HICs. A decision will need to be made on steps required to achieve the 90% full or equivalent conditions. Operations provided some options but they need clarification and direction from ECO/Waste Support Services to perform the work.

> Actionees: Nancy Ware/Tad Karschni. Questions to resolve include:
>
> - Can waste packages <90% full be accepted into MWDUs at all (HTGR drums were void filled prior to placement in the disposal cell)?
> - Can the void filling occur in cell?
> - Can the intent of 90% full rule (i.e., subsidence control) be achieved by some other means such as placement in a HIC or using extra grout/structural monolith.

Operations have provided several options depending on the outcome of the regulatory approval for meeting 90% full. They are:

- Place <90% full waste packages in MWDU, remove the lids, and flood grout to meet 90% full/50 psi/radiological stabilization.
- Place <90% full waste packages in MWDU, cut holes in sides of drums, and flood grout to meet 90% full/50 psi/radiological stabilization.
- Place <90% full waste packages in MWDU, keep packages intact, and use extra grout thickness to meet 90% full/50 psi/radiological stabilization.
- Place <90% full waste packages in MWDU, place in HIC, and void fill to meet 90% full/50 psi/radiological stabilization. This option would require approval to load in <90% drums.

ECOs and Tony Miskho believe they can get CHPRC Environmental Group to approve placement without void filling, then we could choose any pathway agreeable to Operations to meet the 50 psi requirement (monolith/HIC). I will check with them next week if they have made any decisions. Operations will need to know how the drums will be handled regarding the 90% full issue, the they can do their part.

Project information and documents are located on the share drive at Y:\Nester\Contracts\MLLW-07\ANL-E MLLW-07 Drums\ARGON Waste LDR Variance.

Thanks,

Chad D. Cornelison
CHPRC Waste Disposition Project
phone: 509-373-3128
fax: 509-372-0437

ATTACHMENT 3

CONSERVATIVE CALCULATION OF CR IN TCLP EXTRACT IN ARGONNE WASTE

Basis:

1. Primary can and the primary can contents considered waste. All other material considered packaging.
2. Dissolver solution included the dissolved fuel and an Inconel X plenum hardware. Cladding hulls were cemented separately from dissolved fuel.

Givens:

1. 700 liters of waste solution mixed with cement. (Reference 1)
2. Waste cans are 1.5 gallons. (Reference 1)
3. 233 Waste cans were generated. (Reference 2)
4. Waste cans were filled to the top with cemented waste. (Reference 1)
5. Maximum Cr content in Inconel X is 17% maximum. (Reference 3)
6. Maximum Cr content in Zircaloy-4 is 0.13 wt. %. (Reference 4)
7. Maximum Cd content in Zircaloy-4 is 0.00005 wt. %. (Reference 4)
8. Pb is not listed as an impurity in the Technical Data Sheets for both the Zircaloy -4 and the Inconel X. Consequently, it is assumed that any lead present would trival.
9. Summary of fuel data (Reference 2)

Rod	Type	BAPL NiCrFe nominal Mass (g)	Plenum Seg. Mass (g)	Recovered Hulls Mass (g)	Mass Dissolved (g)	
B	PFB	120	186.83	83.174	103.7	
C	PFB	120	186.73	86.737	100.0	
D	PFB	120	185.411	105.144	80.3	
E	PFB	120	189.183	85.687	103.5	
F	PFB	120	187.804	78.09	109.7	
G	PFB	120	186.33	82.953	103.4	
H	REF	120	278.607	188.763	89.8	
I	SB	140	223.316	106.547	116.8	
J	SB	140	224.443	86.452	138.0	
K	SB	140	224.629	78.732	145.9	
L	SB	140	224.433	81.936	142.5	
M	Seed	20	48.252	24.635	23.6	
N	Seed	20	48.018	24.944	23.1	
O	Seed	20	57.745	34.09	23.7	
P	Seed	20	48.917	23.66	25.3	Est.
Q	Seed	20	57.324	30.999	26.3	
R	REF	120	261.634	172.892	88.7	
			Total Mass Dissolved =		1444.2	

Assumption:

1. For a worse case analysis, assume all dissolved material is 17 wt. % Cr (i.e., primarily plenum Inconel components).
2. For a worse case analysis, assume all dissolved material is .00005 wt. % Cd (i.e., primarily cladding)
3. Dissolved material has same concentration as original material.
4. Density of cemented waste is 122.86 lbs/ft3 (Calculated Value).

Calculations:

Maximum possible dissolved Cr =	246 g		
Total Volume of Waste =	349.5 gal	=	46.73 ft^3
Total Mass of Waste =	5741.02 lbs	=	2,604,069 g
Cr content in waste =	9.4279E-05 g/g	=	94.28 ppm

If TCLP extract is conducted (100 g sample/2,000 ml extraction fluid)

Cr in sample = 0.009428 g

Assume a density of 1 ml/g for the extract (this is a conservative estimate) and assuming all Cr leaches out

The Cr conc in the extract = 4.71395E-06 g Cr/g extract = 4.7 ppm

Maximum possible dissolved Cd =	7.E-04 g		
Total Volume of Waste =	349.5 gal	=	46.73 ft^3
Total Mass of Waste =	5741.02 lbs	=	2,604,069 g
Cd content in waste =	2.77291E-10 g/g	=	0.000277 ppm

If TCLP extract is conducted (100 g sample/2,000 ml extraction fluid)

Cd in sample = 2.77E-08 g

Assume a density of 1 ml/g for the extract (this is a conservative estimate) and assuming all Cd leaches out

The Cd conc in the extract = 1.38646E-11 g Cr/g extract = 1.4E-05 ppm

References:

1. "Final Report for the Light Water Breeder Reactor Proof-of Breeding Analytical Support Project," ANL-87-2, Graczyk, D.G., Hoh, J.C., Martino, F.J., Nelson, R.E., Osudar, J., and Levitz, N.M., Argonne National Laboratory.
2. E-mail from D.G. Graczyk to J.D Dalton Dated 5/5/08.
3. Inconel X Technical Data Sheet
4. Zircaloy Technical Data Sheet from ATI Wah Chang, Albany, OR.

Adjusted Calculation using steel and concrete packaging components in net waste weight

Average Net Waste Weight =	**620 kg**	**(Total of 42 drums, 55-gal drum tare = 27 kg)**	
52% is lead shielding and not included =	**322.4 kg**	**322,400 g**	
48% is cemented waste, steel, concrete =	**297.6 kg**	**297,600 g**	
Max possible dissolved Cr =	**246 g**	**per drum =**	**5.86 g**
Cr Content in waste =	**1.97E-05 g/g**	**19.7 ppm**	

If TCLP extract is conducted (100 g sample/2,000 ml extraction fluid)

Cr in sample = 0.002 g

Assume a density of 1 ml/g for the extract (this is a conservative estimate) and assuming all Cr leach

The Cr conc in the extract = 9.85E-07 g Cr/g extract = 1.0 ppm

ATTACHMENT 4

Distribution Category:
Light Water Reactor Technology
(UC-78)

ANL-87-2

ARGONNE NATIONAL LABORATORY
9700 South Cass Avenue
Argonne, Illinois 60439

FINAL REPORT FOR THE LIGHT WATER BREEDER REACTOR PROOF-OF-BREEDING ANALYTICAL SUPPORT PROJECT

by

D. G. Graczyk, J. C. Hoh, F. J. Martino, R. E. Nelson,
John Osudar, and N. M. Levitz

Chemical Technology Division

May 1987

sampled. One tubing section was long enough to be inserted into the BT through the wide-bore gate valve on the tank; the other end of this tubing protruded through the stopper by a length equal to the height of the void space in a properly filled bottle (about 25 mL, or 35 g, of solution was taken for each sample). The other section of tubing extended only to the bottom of the rubber stopper, and connected to the peristaltic pump. The pump moved only air into or out of the sample bottle. Solution from the BT was drawn into the bottle by pumping air out of the bottle; when the protruding end of the inlet tube was submerged in solution, the pump was reversed, and air pressure in the bottle returned excess solution to the BT, clearing the inlet tube of liquid. The stopper/tubing assembly could then be moved to another bottle and the process repeated.

A major advantage of not pumping the solution directly was that tubing in the pump heads did not have to be replaced to provide clean sampling lines; frequent remote assembly and disassembly of the peristaltic pump heads would have been an onerous task. The stopper/tubing assemblies used on this system were prepared en masse outside the hot cell and transferred in as needed.

The bottles used to contain the solution samples are also worthy of note. We selected round, 60-mL Pyrex bottles with a narrow-mouth screw cap closure. Polypropylene caps were used on the bottles after early testing showed that Bakelite caps changed weight with changes in ambient conditions, possibly because wood flour is used as a filler in their manufacture. The polypropylene caps were, in addition, modified to permit venting of radiolytically produced gases generated in the solutions. This modification was made to avoid pressure buildup in samples placed in archive storage. To provide the venting, a small (1/16-in. dia) hole was drilled in each cap and a liner, consisting of a gas-permeable membrane and a Viton sealing gasket, was inserted against the inside of the cap.

With 25 mL of solution, a bottle could be laid on its side without having solution enter the bottle neck; liquids did not easily penetrate the gas-permeable membrane, even with the bottle held upside down. Of course, the solution samples were not intentionally handled in such ways, but selections were made to accommodate worst-case situations.

e. Liquid-Waste Storage System

Provision was made for storing, in the DDS hot cell, the fuel-bearing waste solution produced by the dissolvers. The liquid-waste storage system centered around two 370-L SS waste tanks located between the two dissolver systems. Each tank rested in a deep secondary tray and was enclosed with lead cover plates (1.0-in. thick) to shield the in-cell equipment and thereby minimize damage to radiation-sensitive items. Each tank was also equipped with an externally controlled mixing system and instrumentation to measure liquid level. The vapor space of each tank was continuously purged with house-supplied air to enhance the evaporation of stored solution and thereby reduce the amount of liquid waste needing to be processed into cement waste. A vent delay was incorporated into the air outlet to allow for the holdup and decay of ^{220}Rn (a daughter of ^{232}U), which emanated from the waste solution.

The two waste tanks were connected to a system of valves, which allowed a common transfer pump to be used in moving solution from either BT

to either waste tank, from one waste tank to another, or from either waste tank to the waste treatment facility located on the floor above.

f. Weighing Systems in the DDS Facility

The DDS facility contained five remotely operated electronic balances. Two of these were included as part of the BT assemblies as described in Section III.A.4.a; each BT balance had a set of three 5-kg standard weights fabricated at ANL (see Section III.A.2.d for fabrication details). The other three balances were located in balance wells in the cell work table as described in Section III.A.2.d. These included two PK-300 balances (one at each dissolver work station), which were used to weigh segments (<286 g) and solution samples. The remaining balance was a PK-2000 unit used for weighing segments of mass greater than 286 g prior to their dissolution; this balance was located near the general-purpose work station of the DDS cell.

5. The Analytical Hot Cell

The Analytical Hot Cell was a kilocurie cell having two work stations and was equipped for preparing samples, generated in the POB operations, for analysis. These preparations included such operations as dividing solution samples into weighed aliquots, performing solvent extraction and ion-exchange separations, and carrying out a variety of chemical transformations on samples and solutions. The cell contained two top-loading electronic balances: one, used for coarse weighings, was a Mettler Model PR-700 (dual range, either 70-g capacity at 0.01-g resolution or 700-g capacity at 0.1-g resolution); the other was a remotely operated Model AK-160 (160-g capacity at 0.1-mg resolution), which was located in a balance well with draft shield and interfaced to the project data system. The AK-160 balance was used for weighing the samples and aliquots. Two large-surface hot plates, a clinical centrifuge, and a variety of reagent dispensers and sample-handling fixtures also were in the cell.

In addition to the transfer systems installed in the alpha barrier (see Section III.A.2.b), this cell also had a double-door sliding transfer hatch built into one of its shielding walls. The transfer hatch was a 10 by 12 in. opening in the cell wall, with pneumatically powered shielding doors covering the in-cell and out-of-cell faces of the opening. The door controls were interlocked so that only one of the two shielding doors could be open at any time. To provide easy access to transferred items, the opening had a sliding tray that could be extended into or out of the cell (when the appropriate door was open). A Lexan and steel transfer box, equipped with two glove ports and a SS bottom tray, was attached to the outer cell wall over the shielded transfer hatch opening. The transfer box was vented into the cell and served as an interface in transferring miscellaneous small items such as beakers, ion-exchange columns, etc., into the cell. In addition, it was used for moving prepared samples out of the cell to other analytical facilities. A shielded area for temporarily storing prepared samples (e.g., samples for gamma-counting analysis) was constructed from lead bricks on the floor of the transfer box.

6. The Waste Treatment Facility

A "hot cement" works was set up to dispose of analytic residues (mainly, the bulk dissolver solution) as a monolithic TRU waste form. The cell directly above the DDS cell was selected for the waste treatment operation to

simplify transfer-piping installation. The cell was partitioned so that it formed an L-shaped alpha-containment region, which was further divided to separate each leg of the "L." Each cell area served a different function. The larger area housed two specially designed mixing stations, a transfer lock for moving materials into the cell, and a specially designed "can-out system" for removal of cement-filled cans, which comprised the monolithic waste. The smaller area contained 10 drying ovens (see process description below). The barrier wall separating these two regions was fitted with a transfer lock but also allowed for directed ventilation flow (also discussed below). All of the equipment was designed to be maintained remotely with M/S manipulators. Because waste treatment operations did not affect the validity of ANL's destructive assay results, discussion of this topic is kept brief in this report. Consequently, facilities, operations, and results are all described in this section (III.A.6), rather than being separately considered as is done for the other major operations areas (FSS, DDS, Analytical).

a. Equipment

(1) The Cement Mixing Stations

The two cement mixing stations were designed and built at ANL. Basically, they were Unistrut-framed, Lexan plastic boxes, each fitted with a relatively tight-fitting, gasketed door. Box features included a specially designed paddle for efficient mixing in the paint-can type primary containers; the paddle was driven by a gear transmission drive. A fixed, water-cooled reflux condenser was mated to a portable spool section that was brought in with the primary can; this minimized acid vapor release to the cell ventilation system (and cell stack). A pneumatically driven sliding/lifting platform raised the primary can into place for mixing.

(2) Auxiliary Equipment

Auxiliary equipment included an acid-feed system for slowly adding waste solution to the cement during mixing and 10 drying ovens for dehydrating the cement product. The feed system was built around two 11-L acid-feed reservoirs, each fitted with liquid level probes and an adjustable overflow line so that the liquid inventory could be limited to the desired quantity, nominally about 2.5 to 3.0 L; excess liquid was returned directly to the waste storage tanks in the DDS cell. Peristaltic pumps transferred the acid waste from the DDS cell up to the feed tanks in the cement-making cell and metered the solution sent to the cement mixing station. Two simple beam balances monitored water removal in the course of the setting and drying steps.

The drying ovens (product of Sybron/Thermolyne, Dubuque, IA, Model No. 0V19225) operated from 120-V AC line voltage with a power rating of 350 W. Each oven was modified to facilitate remote operation and repair. The door latch was replaced with one that could be more easily operated with M/S manipulators; the heating element was mounted in a drawer that could be easily slid into or out of the oven cabinet while the element connectors were being aligned; and the oven thermostat was removed, temperature control being provided by an out-of-cell controller connected to a thermocouple that was installed in the oven.

b. The Waste-Cement-Making Process

The process for making the cemented waste evolved after a review of literature, evaluation of waste disposal options, and laboratory formulation studies. This process is considered unique in at least two ways: (1) thin-walled steel cans were used for the disposal of a 10-N acidic (HNO_3-HF) solution; and (2) the filled cans, after setting, were dried (at 125°C) to reduce the residual water content so that pressurization due to radiolysis effects would not present a hazard.

The several-step process is outlined below.

(1) A weighed cement-water-lime slurry containing small amounts of two commercial additives, an anti-slumping agent, and a set retardant is premixed in a nominally 1.5-gal steel can (similar to a paint can).

(2) The can (with lid) is transferred into the mixing area of the cell by way of the transfer hatch. A specially designed can lifter is used with the manipulators because the cans have no bails (a space-saving feature for the packaging step).

(3) A spool piece for connecting to the condenser in the mixing station is placed on the can, and the can is placed in the mixing station and raised into position for the acid-addition mixing step.

(4) A 2.8-L batch of waste solution is transferred up from the waste storage tank in the DDS cell to the appropriate hold tank in the cement-making cell.

(5) The mixer is turned on, and the acid feed started. (The duration of the feeding period was reduced from three to two hours during the course of the waste work-off. A magnetically held surface thermometer on the side of the can monitors the temperature of the mix; temperatures to 90°C were observed.)

(6) After the mixing step, the can is weighed and set aside for the contents to set, nominally for three days.

(7) The can is then weighed again and oven-dried (at 125°C) for four days.

(8) Several cans are accumulated, and subsequently topped-off with additional hot mix to increase the overall waste loading per can. (Loading is increased ~25% by this step.)

(9) The topped-off cans are again allowed to set and then given a final drying for up to seven days, or until a constant weight is achieved.

Interlocks and other safety features were incorporated to ensure safety in carrying out the process, as follows:

(1) The platform could not be raised unless the door to the mixing box was fully closed and latched.

(2) A mechanically set restraining pin was used to lock the platform in the "up" position; thus, in the event of air failure, the platform would not slide down while mixing was in progress.

(3) The acid feed pump and holding tank outlet valve were automatically shut off if the mixing motor stopped. An audible alarm was included in this system.

(4) A float-type liquid sensor in the drip pan under the acid-feed pump also halted the acid feed and shut off the pump in the event of liquid buildup due to leakage.

c. Operations

Actual cement-making operations were started on November 11, 1984, and continued through October 1986. Some 700 L of waste dissolver solution, producing ~230 cans of waste, was disposed of. In addition, the cement approach was used to dispose of non-transuranic (TRU) wastes, e.g., Zircaloy hull residues from the dissolver operations (mixed with cement in a 1:1 weight ratio), and a basic aluminum nitrate solution from the analytical cell. For the non-TRU wastes, the mixing was done by hand (i.e., with the manipulator and a paddle) rather than in the mixing station.

Operations were generally smooth, except for one recurring problem, namely, plastic tubing failure, either in the peristaltic pumps or at end-fittings. The tubing apparently degraded due to the severe conditions, i.e., radioactivity plus strong acid. Its failure resulted in leakage, generally requiring localized cleanup (tissue mop-ups), which created another small waste stream. In time, a maintenance schedule was established to periodically change the pump line, but even this precaution did not prevent failures occurring from time to time.

Simple and effective means for disposing of three side waste streams were developed during the course of the cement-making operations. Disposal of tissue used in wiping up solution spills was first attempted by forcing the bulky wads of paper into wet cement in the primary waste cans. This proved quite awkward when working with manipulators. The alternative route explored was thermal degradation. Bench tests showed that tissues degraded essentially to a powder at about 140°C. Since our drying ovens had a limit of about that level, it was a simple task to loosely wad dried tissue into an empty waste can in the cell, heat the material for a few hours, and then use this can, which contained the degradation product and a small amount of associated nitrate salts, to prepare a normal can of waste. This method proved successful.

Cans used in preparing the cement with which other cans were topped off accumulated in the cell and represented the second side waste stream. To dispose of these cans, we began preparing the starting cement slurry in-cell

with these cans. The dry slurry components were brought into the cell in plastic pouches, and a water supply for forming the slurry was provided. After some preliminary "hand" mixing of the slurry in a given can, the can was installed in one of the mixing stations where it was treated as described earlier. All cans that had accumulated inside the cell during early waste disposal work were disposed of in this manner.

A third side waste-stream was the plastic pouches used in transferring the slurry components and other polyvinyl-chloride-plastic waste material. Again, the drying ovens served a useful purpose because the plastic had a relatively low melting point. The plastic was loaded into an empty can and the contents were heated for about two hours, giving a consolidated, rather high-density mass (much like a cake of wax), readily disposed of as a radioactive, but non-TRU waste. No problems were encountered with off-gasses from the plastic.

d. Packaging the Waste

To facilitate disposal of the waste at an away-from-ANL repository, a waste package ("package" refers to the item placed in actual storage at the repository) was designed to meet requirements for TRU waste storage at the federal Waste Isolation Pilot Plant (WIPP). The requirements include use of two alpha seals, limited (to 7 psig) pressurization potential, and use of approved containers. Further, for contact-handled waste, radiation levels at the surface of the package had to read <200 mR/h. Because our primary cans of waste gave readings of ~250 R/h, a shielding cask was necessary (see below).

The package included the following:

(1) Two sealed primary cans loaded vertically into a secondary can (similar to a paint can). The lid on the secondary can serves as one of the two alpha seals.

(2) A steel shielding cask that provides a snug-fitting cavity for the loaded secondary can and has about 2.5 in. of lead shielding. The lid on the cask is bolted but not gasketed.

(3) The outer container, an approved (DOT-17C) galvanized 55-gal drum.

Shipment to an interim storage site was necessary because the WIPP has not been completed; the drums were loaded into Polypanther (trademark) overpacks, six to a truck, and are being sent to Rockwell-Hanford, which can store the waste for up to 25 years.

B. Analytical Facilities

Facilities associated with the ACL and used in the POB project included four laboratories equipped for general or specialized analytical chemistry operations and an alpha/gamma counting station installed at the Analytical Hot Cell specifically for use with project samples. The laboratory facilities included (1) a general-purpose laboratory for preparing chemical standards and reagents needed in project operations, (2) a Uranium Purification Laboratory set up for isolating and

built-in software interlocks to prevent the operator from activating certain critical process-control states under conditions that could jeopardize the validity of analytical results obtained for the segment being dissolved. In a few cases, the need for additional interlocks during specific operations was not recognized until after operational mishaps had occurred. (See Section V.C.3.b for a discussion of operational mishaps during the dissolutions of LWBR fuel rod segments and successful recovery actions that were taken to deal with them.) The IPC programs were subsequently modified as appropriate during the EOL campaign to guard against recurrence of each type of problem that arose.

Owing to the graphical displays in the computerized dissolver operations, the operator could examine the status of system components or monitor the progress of a particular operation (e.g., heatup or cool down of a dissolver vessel or BT) in a straightforward, easy-to-read format. Examples of the P&I diagrams and plots that were available for display are shown in Fig. 16. Appropriate displays were called up by the OPRDSx programs during certain automated procedure steps; any of the displays could also be called up by operator command at the work station terminal, as desired. Data used in the plotting displays were stored in special computer files regardless of whether or not the display was active at the time the operations portrayed in the plot were carried out. The data in these files could be plotted at any time, on command, so that the dissolver operator could switch between displays without losing information, or the operations could be reviewed after they were complete.

Data acquired by the computer system during each segment dissolution, including operator sign-off information, alarm messages, and operator comments, were recorded in a manner analogous to that used at the FSSF. Detailed information was recorded in a computerized process log (both computer file and printed versions), and selected information was stored in a computerized data summary file for subsequent use in generating reports. Several manual logbooks were also maintained at the DDS work stations. A manual operations logbook was kept for each dissolver station, in which operator comments and actions, important data, unusual occurrences, etc., were noted on a segment basis. A separate, general operations log was also kept at the work area to note activities related to the entire DDS facility. Specific routine activities were documented in supplemental logbooks titled according to the activity, e.g., Equipment Maintenance, Sample Movement, and Fissile Material Inventory. Complete, redundant records, as provided by this data management system, formed the foundation for quality assurance within the project.

The OPRDSx procedure for dissolving segments in the DDS dissolver systems recognized three types of segment on the basis of the segment identification number: (1) a fuel-bearing segment, identification number in the range 01 to 17; (2) a plenum segment, number 00; and (3) a dummy segment, number in the range 91 to 99. Details of the dissolution sequence were automatically varied by the procedure programs to correspond to the type of segment being dissolved.

3. The DDS Operating Procedure

The DDS operating procedure had five major sections: (1) preliminary equipment checks and installations of equipment items, (2) the two-stage dissolution of the segment, (3) sampling of the dissolver off-gas, (4) BT

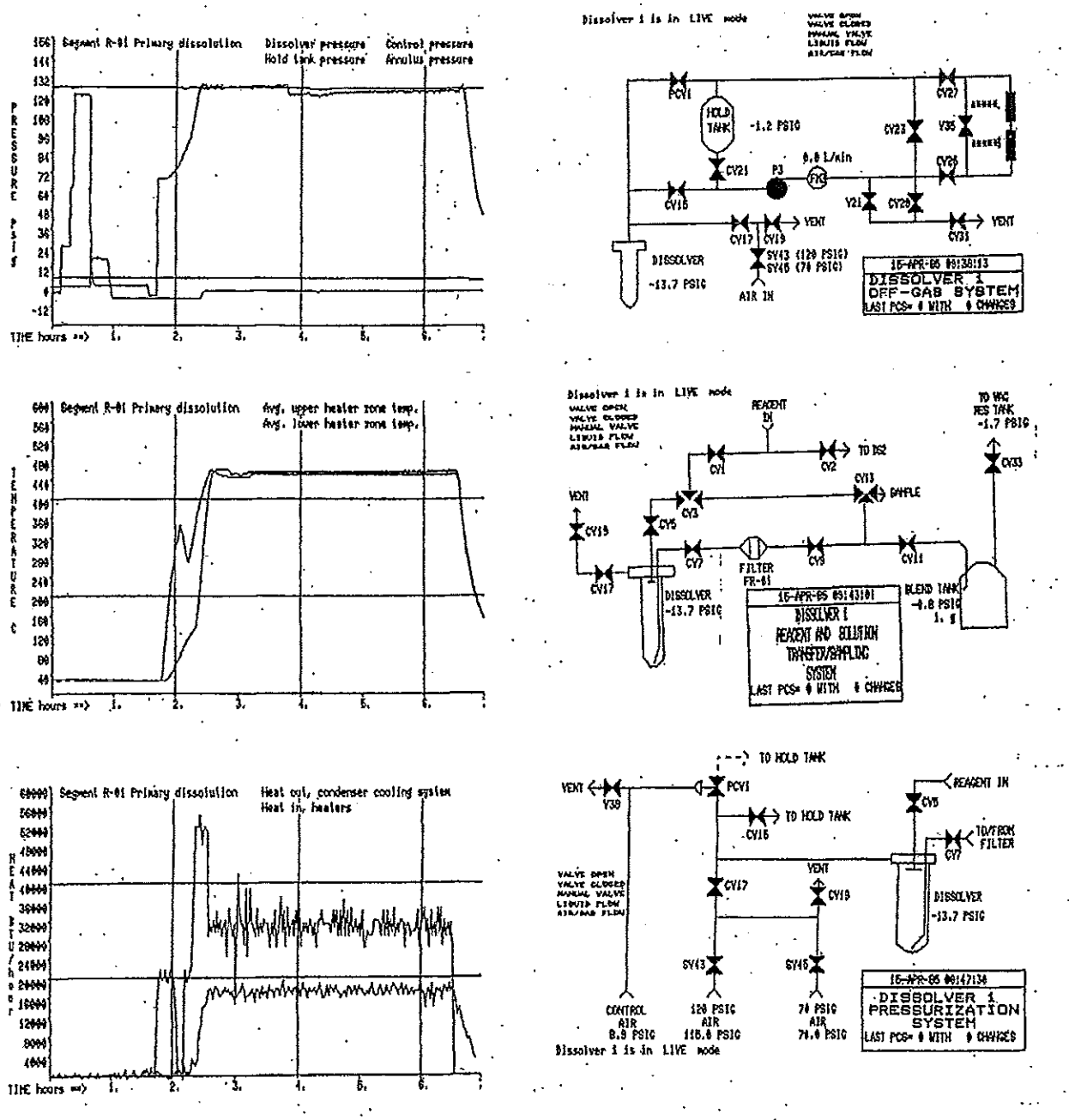


Fig. 16. Examples of Dissolver System Graphics

operations, and (5) post-dissolution operations, such as recovery of the segment's cladding hulls and decontamination of reusable equipment. All of these operations were carried out for each fuel-bearing segment. For plenum and dummy segments (i.e., cleanup dissolutions), certain operations were automatically omitted or modified by OPRDSx to streamline the process; these exceptions are identified in the appropriate subsections. A complete dissolution for a fuel-bearing rod section required 30 to 48 h.

a. Preliminary Operations

In preparation for a given dissolution, operations were carried out to check performance of the equipment and to provide the needed materials; these operations are discussed below.

(1) Balance Tests

The in-cell balances to be used during dissolution of a given segment were first calibrated with the in-cell standard weights and then individually tested for linearity, precision, and stability by means of the BALQA balance-test program [Section III.C.2.c.(1)]. Each time one of these balances was specified for use during subsequent operations, OPRDSx checked the computerized record of tests performed on the balance and determined the time since the last successful BALQA test was run. If the prescribed balance had not passed BALQA within the previous 48 h, OPRDSx automatically brought up the BALQA program for the operator to execute before proceeding with the weighing operations.

In a similar fashion, the short calibration-check program, BALCC, was brought up by OPRDSx just prior to each weighing operation in the procedure, even if the requirement on BALQA was satisfied. If the balance failed the BALCC check, BALQA was, again, brought up automatically for the operator to run as an aid in diagnosing the reason for the failure. These precautions helped assure the validity of weighing data obtained during each DDS operation.

Although the same balance-testing procedures were used in the FSSF and DDS (cf. Section IV.D.1.b. for the FSSF operations), the timing of the tests and the tolerances applied were different for the two facilities so that the specific analytical and operational needs of the respective use of the balances could be accommodated.

(2) Weighing of Sample Bottles

Another preliminary operation to each segment dissolution was the weighing, both outside the cell and inside, of individual empty glass bottles, used for sampling the dissolver solutions. This was done to establish a tare value for each sample taken. Prior to weighing, each individual bottle and its cap were labeled with the identification code of the sample for which it was to be used; the bottle and cap were weighed together in determining the empty-bottle weight.

During the weighing routines, the computer prompted the operator to weigh, in triplicate, to the nearest milligram, the appropriate number of bottles for the type of segment dissolution being performed, i.e., ten bottles for a fuel-bearing segment, four bottles for a plenum segment, or two bottles for a blank run. The computer called for each bottle on the basis of the identification code on its label; such specific prompting by the computer was made possible by the standardized sample nomenclature described in Section IV.A.

The OPRDSx routine for weighing the bottles inside the cell also compared the in-cell weight of each bottle with the out-of-cell weight and advised the operator concerning the significance of any differences that were

detected. This comparison served to check the performance of the in-cell balance, as well as to reduce the chance that the sample bottles had been mixed up during one or the other weighing. The out-of-cell bottle weights were recorded in a special computer file; the in-cell weights and the differences between the in-cell and out-of-cell weights were recorded in the dissolution process log and the dissolver data summary file.

(3) Installation of Filter Assembly, Gas-Sampling Cylinders, and BT

For each segment dissolution, we installed fresh auxiliary components in the dissolver system, including the filter assembly in the solution transfer line, gas cylinders used to obtain samples of the dissolver off-gas, and a BT. Before this installation, the OPRDSx program instructed the operator to select the component predesignated in the FRIF for use with the given segment and, by reading the HISLOG file, it verified that the component had been appropriately decontaminated and tested for reuse since its last previous use in the system. The decontamination procedures for the filter assemblies and BTs are described in Section IV.E.3.f.(1) and (2). If any of the designated components were not verified as ready-to-use, the operator was able to make a suitable substitution; the substitute component was also checked by the program to verify its acceptability. When the components were accepted, their identities were automatically recorded in the process log and data summary for the segment being processed. The operator was then instructed to install the components.

Installation of the BT included weighing of the BT support assembly, both with and without the tank in place; each weighing was made in triplicate. The weight of the complete assembly was stored in the computer for use in computing net weights of solution in the BT during subsequent operations; the difference between the weights with and without the BT was taken as the weight of the empty BT itself. The empty BT weight was recorded in the process log, the dissolution data summary, and the HISLOG file for that BT. The HISLOG record of empty weights for each of the nine reusable BTs served as a means of monitoring corrosion of the tanks with use; weight changes for the BTs proved insignificant over the duration of the EOL campaign, suggesting minimal corrosion.

Gas-sampling cylinders were required only for dissolutions involving fuel-bearing segments. In the case of plenum or blank dissolutions, where off-gas was not sampled, the operator was instructed to install a jumper connector in the off-gas sampling line in place of the gas-sampling cylinders.

(4) Loading of the Segment into the Dissolver Vessel

After the installations of the components, the operator was prompted by OPRDSx through a check of the helium and air supply systems associated with the dissolver system and then was instructed to load the segment (in its capped aluminum can) into the dissolver vessel. The operator first retrieved the specified segment from the shielded segment-storage area and weighed the segment on the appropriate (i.e., 300-g or 2000-g capacity) balance. The computer compared the result of this weighing with the appropriate full-can weight logged during FSSF operations as a means to verify the identity of the segment. If the DDS and FSSF weights did not agree within predetermined limits (a situation that did not arise during actual EOL operations), the operator

was instructed to double-check the identity of the selected segment and to enter a comment to the computerized log before proceeding. As an additional quality assurance (QA) check to verify the identity of the segment before it was dissolved, the operator was prompted to have the shift supervisor enter the identity of the segment being prepared for dissolution. If the supervisor's entry did not agree with the information previously entered to OPRDSx, the program indicated the discrepancy and required an additional entry by the supervisor, acknowledging that the discrepancy had been resolved. Once the problem had been solved, operations could proceed. The segment identity, the FSSF and DDS segment weights, and the weight difference were automatically written to the process log and the dissolver data summary file.

Before the segment was placed in the dissolver, the cap of the aluminum sample can was punctured with a specially built device. The purpose was to equalize the pressure when the dissolver vessel was pressurized and depressurized during pre-dissolution operations. This prevented the can from being deformed and allowed its retrieval, intact, if some mishap that required drastic action occurred during these preliminary operations.

To load the segment, we removed the dissolver cover flange and installed a new flange gasket. The segment was then locked into the tantalum dissolver basket and lowered into the vessel. The vessel was sealed by bolting the cover flange in place.

(5) Pre-Dissolution Leak Testing

Once the segment was loaded into the dissolver vessel and the vessel was sealed, the computer carried out a series of fully automated leak tests on the dissolver vessel, the BT assembly, the filter assembly, and the off-gas system. In each test, an appropriate portion of the dissolver system was either pressurized or evacuated, and the pressure was monitored at specified intervals (usually 5 to 10 seconds) over a preset period of time. If the pressure changed by more than a prescribed tolerance during the test, or if the prescribed starting pressure for the test could not be attained, the computer notified the operator that a leak was present and that the leak should be repaired and the test repeated.

The dissolver vessel was pressurized with air to 120 psig for the test and was required to lose no more than 2 psig in 15 min to pass the leak test. The air from the dissolver vessel was then transferred to the off-gas system and used to pressure-test it. The off-gas system was required to lose no more than 1 psig pressure, from a starting pressure of not less than 10 psig, during a five-minute recirculation of the gas in the system. The BT and filter assemblies were tested under static vacuum at -9 psig or less. The BT assembly was judged acceptable if its pressure did not increase by more than 0.5 psig in five minutes. The filter-assembly pressure had to increase by not more than 0.5 psig over a two-minute period to be judged satisfactory. When all the components had successfully passed their leak tests, dissolution of the segment was begun.

b. Two-Stage Segment Dissolution

Dissolution of each fuel-bearing segment was a two-stage process in which the segment was subjected to a primary and then a secondary contacting with dissolvent at elevated pressure and temperature. After each contacting, the solution in the dissolver was transferred into the BT and the dissolver vessel was given a special rinse treatment; each rinse solution was also transferred to the BT. Samples of the solution from the secondary contacting were taken, during transfer of the solution to the BT, to assess the completeness of segment dissolution. Gases collected in the dissolver off-gas system during the primary contacting were also sampled to determine the fission gases that were released by dissolving the segment.

In carrying out these operations, the OPRDSx computer programs alternated between interactive sequences, in which the DDS operators were instructed to perform specific manual manipulations, and fully automated sequences wherein the computer (1) monitored key sensors to evaluate the status of operations and initiated progressive stages of the process, (2) performed process-control activities to configure valves, etc., in a manner appropriate to the operations at hand, and (3) calculated heat and material balances to aid the operators in tracking progress of the operations and performance of the equipment. Operating conditions and sequences for the primary and secondary dissolutions are described below; sampling of the dissolver off-gas is discussed in Section IV.E.3.c.

Three different reagents were used in the DDS operations: Thorex reagent (13.6M HNO_3, 0.06M HF with Cs and Ce carriers at 1 μg/mL concentration); Thorex-Al reagent (identical to Thorex, but containing 0.06M Al^{3+}); and dilute (0.5M) nitric acid used as a rinse solution. The Cs and Ce carriers in the Thorex reagents prevented adsorptive losses of these fission-product elements from the fuel solution. The Al^{3+} in the Thorex-Al solution complexed the fluoride ion during the secondary dissolution (for which the Thorex-Al reagent was used), and thereby inhibited corrosion of the tantalum vessel. The aluminum from the segment sample can served the same purpose in the primary dissolution, where the standard Thorex reagent was employed.

Each reagent was prepared in 50-L batches by the ACL and was introduced to the DDS through the reagent-charging station. Each batch was analyzed, at the time it was prepared, to verify its composition and to demonstrate the absence of significant uranium impurities. Details of the preparations and analyses are given in Document C-0030-0286 (see Attachment 1). The ACL issued a certificate of analysis for each reagent batch, which listed the results of the composition verification, as well as other information pertinent to the traceability of the data (see Attachment 2 for examples of these certificates).

(1) Primary Dissolution

For all primary dissolutions, the segment was contacted with Thorex reagent at 195°C under 120 psig pressure for four hours; for blank dissolution runs, the primary dissolution was omitted completely. The volume of Thorex used for any given segment was specified in the FRIF and was based on segment type, weight of fuel material, and experience gained during prior

dissolutions of similar segments. Thorex volumes ranged from 1.0 to 3.5 L for the LWBR fuel rod segments. Upon completion of the primary dissolution, the solution was transferred to the BT, and the dissolver vessel was rinsed by refluxing 750 mL of dilute nitric acid for 15 min at 100°C under 10 psig pressure. This reflux-rinse solution was also transferred to the BT.

In carrying out the primary dissolution, the OPRDSx program first referred to the FRIF to identify the Thorex volume specified for the segment being dissolved and then instructed the operator to dispense the appropriate weight (computed using the Thorex density) of Thorex reagent into the charging vessel at the reagent-charging station. After the reagent dispensing was complete, the operator was requested to enter the type of reagent (entry checked to verify "Thorex"), the batch number of the Thorex used, and the weight of reagent dispensed. Each entry was recorded in the computerized log and data summary file.

Upon accepting the reagent identity and quantity, the computer (1) automatically checked specific sensors to verify that the dissolver was in proper condition to receive reagent, (2) energized the appropriate process-control state to transfer reagent into the dissolver vessel through the spray ring, (3) displayed the appropriate P&I diagram on the graphics terminal, and (4) pumped the Thorex from the charging station to the dissolver vessel. It then checked the dome-valve control pressure and air supply pressures, pressurized the dissolver with 70 psig air, and initiated full cooling water flow to the condenser. When satisfactory execution of each operation was verified, the operator was instructed to turn on the heater controls and reset the kilowatt-hour (kW-h) meter for the dissolver system. When the operator acknowledged completion of these steps, the program began a fully automated heatup procedure.

For the heatup sequence, the program preset alarm criteria for specific sensors in the system, displayed a real-time plot of temperature vs. time on the graphics terminal, and then energized the lower-zone (LZ) heaters on the dissolver, monitoring the kW-h meter to determine whether all heaters were functioning and whether adequate heating was available. Abnormally low or inadequate heat flow to the dissolver was called to the operator's attention and corrective action (e.g., stopping the heatup to allow for operator review) was automatically taken as required. Once proper operation of the LZ heaters was verified, the program checked the FRIF to determine whether the upper-zone (UZ) heaters were required for this dissolution. (The UZ heaters were used for Thorex volumes of 3.0 L or greater.) If needed, the UZ heaters were automatically started in a manner analogous to that used for the LZ heaters. The program then entered a sensor monitoring-and-display sequence to track progress of the heatup. When the LZ heater temperature reached a value of 150°C, the operator was instructed to retighten the bolts on the dissolver cover flange; this step in the procedure was added because small vapor leaks were occasionally found at the closure gasket during heatup with the early LWBR fuel rod segments. (The computer system controlled dissolver temperature on the basis of the readings from control thermocouples mounted in the heater assembly and not the actual internal temperature of the dissolver vessel; the dissolution temperature of 195°C corresponded to a heater block temperature of 450°C.)

Heatup of the dissolver vessel was continued until the LZ heater temperature exceeded 400°C, the UZ heater temperature (if used) was greater than 375°C, and the dissolver pressure was at least 115 psig. When these conditions were met, the computer logged the "primary dissolution start time" and automatically proceeded to the next procedure step. In this step, the primary dissolution sensors were displayed and updated, keeping the operator apprised of system temperatures and pressures as well as condenser cooling parameters such as cooling water flow rate and temperature differential ("delta T"). After four hours with the dissolver at temperature and pressure, the heaters were de-energized automatically, and sensor readings were displayed to monitor cool down of the vessel. The end time of the primary dissolution, i.e., the heater cutoff time, was also logged.

When the LZ temperature reached 95°C, the process-control state that vented the dissolver to the off-gas hold tank was automatically energized, and the pressure was allowed to equilibrate. Then, the program twice repressurized the dissolver with 120-psig air and vented it to the hold tank to enhance transfer of the dissolver off-gas to the hold tank. Next, the residual gas in the dissolver freeboard was pumped to the hold tank until the dissolver pressure reached 0 to 2 psig. This sequence of steps ensured virtually complete transfer of the off-gas (including the fission-product gases released during dissolution) to the hold tank and thereby assured representative sampling of the gas for the fission-gas determination.

The computer next instructed the operator to put the BT into the "Transfer Weighing Condition" so that solution could be transferred from the dissolver vessel to the BT. In the Transfer Weighing Condition, all BT lines and cables were disconnected except for the (flexible) connections to the solution-transfer piping and to the vacuum reservoir system; this allowed for free movement of the BT during the subsequent dynamic weighing operation.

When the operator acknowledged that this instruction was carried out, the program proceeded to an automated solution-transfer sequence in which the BT was first evacuated and lowered onto the BT balance, the BT tare weight was recorded, and then the dissolver was vented to the cell atmosphere to transfer the dissolver solution into the BT. The computer monitored the pressure in the BT and the vacuum reservoir and continued the solution transfer until this pressure exceeded -0.5 psig, i.e., until vacuum in the reservoir was exhausted. At this point, the computer read the BT balance, calculated the weight of solution transferred into the BT, and compared this weight with a theoretical solution weight based on the weight of the canned segment, the weight of Thorex added, and the estimated weight of cladding hulls that the segment contained (the hulls were presumed not to dissolve, although, in actuality, hull dissolutions to the extent of 10 to 25% occurred). If the weight of transferred solution accounted for at least 98% of the theoretical weight, the transfer was judged complete, and the percent solution transferred was automatically logged. If the transfer did not provide at least 98% of the theoretical weight, the program automatically repeated the transfer sequence after a 15-min delay to allow decay of ^{220}Rn that might have accumulated in the vacuum reservoir tank. Incomplete recovery after the second try resulted in a prompt to the operator to investigate the cause of the low recovery and take necessary remedial action.

After transfer of the dissolver solution to the BT, the program proceeded directly to reflux rinsing of the dissolver vessel, which was done in a manner completely analogous to the contacting with Thorex. The operator was instructed to dispense the appropriate weight (759 g) of nitric acid rinse solution; the identity, batch number, and weight of solution were logged; the reagent was automatically charged to the dissolver through the spray ring; and then a fully automated heatup, refluxing (lasting 15 min), and cool down of the vessel were executed. The rinse solution, once cooled, was also transferred automatically to the BT as described above for the dissolver solution. In the case of the rinse solution, the theoretical solution weight for the material balance calculations included only the weight of rinse solution that had been added to the dissolver.

The next step in the operating procedure depended on the type of segment being dissolved. For fuel-bearing segments, the operating program continued to the sampling of the collected off-gas (Section IV.E.3.c) and then to the secondary dissolution. For plenum segments, the off-gas was not sampled and the second dissolution was omitted, so that the program branched off to the cold rinse of the dissolver vessel, as described below, at the end of the secondary dissolution sequence.

(2) Secondary Dissolution

For the secondary dissolution, one liter (about 1370 g) of Thorex-Al reagent was added to the dissolver vessel through the dissolver drain line (as opposed to through the internal spray ring) in such a way that the filter in the solution-transfer line was backflushed. This backflushing carried undissolved fuel particles from the filter back to the dissolver vessel.

The secondary dissolution occurred under the same conditions as the primary dissolution but was maintained at pressure and temperature for three hours rather than four. Following the secondary dissolution cool down, just prior to the transfer of the dissolver solution, the computer prompted the operator to prepare for sampling the solution. The operator was instructed to connect a clean, new, disposable sampling line to the sampling port on the solution transfer system and to obtain the two sample bottles designated for secondary dissolution samples. The automated solution transfer was then begun but was automatically interrupted when 500 g of solution (~40% of the total) had been transferred to the BT. At this point, the operator was prompted to obtain samples of the dissolver solution and to weigh the full sample bottles, and the computer recorded the bottle weights. The computer then calculated the net weight of solution in each bottle, recorded this information, and completed the solution transfer. In calculating the percent of the secondary dissolution solution that was recovered in the transfer to the BT, the OPRDSx program included the sum of the net solution weights in each sample as part of the recovered solution. Secondary dissolution samples were not taken for plenum or blank dissolutions.

The above transfer was followed by a 200-mL (hot) reflux rinse with dilute nitric acid and a 250-mL cold rinse; in the latter case, the rinse solution was added to the dissolver vessel through the spray ring and then transferred to the BT without having been heated. At this point, all primary and secondary solutions were present in the BT.

c. Sampling of Dissolver Off-Gas

The off-gas collected during dissolution of each fuel-bearing segment was sampled to determine its fission gas content; other selected components (e.g., NO_x, H_2) were also measured. Off-gas from the dissolution of segments from rod R, the last rod to be processed in the campaign, was not sampled, owing to difficulties with the gas-handling equipment in the DDS hot cell. As a result of frequent failure of the metal-bellows pumps used to transfer and recirculate dissolver off-gas during DDS operations (either through fatigue of the metal bellows or failure of the pump motors), the inventory of spare pumps and spare parts for the pumps was depleted when a failure occurred during processing of rod Q. This failure prompted the installation of a lighter-duty pump, which performed adequately for gas transfers but had trouble recirculating the gas to mix it prior to sampling. Procurement of parts to repair the heavy-duty pump was ruled out because of the long delivery time quoted on the parts and the short time until the end of the campaign. Because of concern that the light-duty pump might fail under the load of gas recirculation and leave the DDS operations without any gas-handling capabilities, ANL asked that BAPL waive its request for sampling and analysis of the off-gas from dissolution of the rod R segments; BAPL acceded to this request.

In general, samples were taken only of the gas from the primary dissolution, in which the bulk (90 to 99%) of the segment fuel was dissolved. Earlier experiences showed that the fission-gas content of the secondary dissolution off-gas represented a negligible fraction of that obtained from the primary and did not merit the effort and cost of its measurement. Before sampling, the gas collected in the off-gas system was thoroughly mixed by recirculating the gas through a closed piping loop that included the off-gas hold tank.

The gas recirculation was automatically initiated by OPRDSx when the operator acknowledged acceptance of the results from the steps just prior to this part of the procedure, i.e., the reflux-rinse solution transfer at the end of the primary dissolution. The gas in the off-gas system was first recirculated through the ~60-L in-cell portion of the loop for 30 min at a 25-L/min flow rate and then was diverted through the sample cylinders attached at the out-of-cell gas-sampling station. Recirculation was continued for a period of 5 min at a flow rate of 20 L/min to flush and fill the cylinders. The two sample cylinders were then isolated, closed, removed from the sampling system, and submitted for analysis. Data pertinent to subsequent calculations of results of the analyses, e.g., the pressure in and temperature of the off-gas hold tank at the time of sampling, were automatically recorded in the process log and the dissolver data summary file.

The gas that remained in the system was slowly vented to the cell air-exhaust system to be diluted with cell air and released to the cell exhaust stack. In carrying out this venting, OPRDSx first displayed the P&I diagram for the off-gas system, energized the appropriate process-control state to vent the off-gas hold tank, logged the time as the start time for off-gas release, and monitored the change in hold-tank pressure as a function of time. The operator was instructed to adjust, as required, the metering valve that controlled the rate of venting to maintain an appropriately low rate of release. When the hold tank pressure reached 1 psig (usually a period of about 2 h), the end time for off-gas

release was automatically logged. Off-gas releases in the DDS were also monitored on the radiation-monitoring system for the exhaust stack.

Except for its not being sampled, dissolver off-gas collected during the secondary dissolution or during dissolution of a plenum segment was treated in identical fashion to that just described.

d. Blend Tank Operations

The next major section of the OPRDSx procedure dealt with weighing, blending, and sampling of the solution in the BT. The solution and rinses accumulated in the BT were blended to provide a homogeneous solution, sampled, spiked with a known amount of NBS 950a standard reference material, and sampled again. The BT assembly and the solution samples were weighed to obtain data required for subsequent analytical calculations and to monitor the material balance during each BT operation.

For each weighing, the BT assembly was first put in the "Standard Weighing Condition" by disconnecting all attached lines, cables, etc., and verifying that it was free of extraneous objects. In this condition, the measured assembly weight could be compared directly to the assembly tare obtained earlier [Section IV.E.3.a.(3)].

The four major BT operations are described below, in the order in which they were carried out.

(1) Blending and Sampling of Unspiked Solution

Upon acceptance by the operator of the computer-calculated material balance, after transfer of the final (cold) rinse that followed the secondary dissolution, OPRDSx proceeded directly into the BT operations, which started with an initial weighing of the unspiked, unmixed, unsampled (UUU) solution. The assembly was then automatically weighed in triplicate to the nearest gram. The automated sequence of operations included raising and lowering the assembly off of and onto the balance for each weighing by means of air-powered pistons on the BT support structure, reading the balance, averaging the results, calculating a net solution weight by subtracting the BT assembly tare weight, and displaying the individual weight values for operator acceptance. When accepted by the operator, all the weighing data were logged automatically.

Next, the solution in the BT was mixed by stirring it for 30 min with the integral stirrer built into the BT assembly. The OPRDSx program prompted the operator through the steps involved in connecting appropriate hoses to the BT, coupling the stirrer to the stirrer motor, and initiating the mixing operation. During the mixing step, the program monitored and displayed the elapsed mixing time, remaining mixing time, vacuum-reservoir pressure and pressure-increase rate, and the pressure in the BT. Any off-normal sensor readings caused an alarm message to be displayed, which instructed the operator to take remedial action. During the mixing step, a slow flow of cell air was drawn through the BT headspace into the vacuum reservoir tank to allow for decay of ^{220}Rn that emanated from the solution. This precaution prevented this gaseous, alpha-emitting radionuclide from being released to the cell atmosphere.

At the end of the mixing period, the BT assembly was automatically weighed to provide a weight of the unspiked, mixed, unsampled (UMU) BT solution. The OPRDSx program calculated this solution weight from the UMU assembly weight and the assembly tare and also calculated the weight of solution lost (as vapor) from the BT during mixing by subtracting the UMU solution weight from the UUU solution weight recorded earlier. Generally, the weight loss on mixing was smaller than could be determined with the BT balance (i.e., less than 1 g). All the measured data and calculated weights were displayed for operator acceptance and logged. The UMU weight of solution in the BT was taken, in subsequent analytical calculations, to be the most representative weight of solution in the unspiked BT.

In the next step, samples of the UMU BT solution were withdrawn for measuring the isotopic composition of uranium in the segment and assaying the segment for fission-product monitors (^{137}Cs, ^{144}Ce, and ^{95}Zr). Four separate samples of the solution were taken in the case of fuel-bearing or plenum segments; only two were taken for blank runs.

In sampling the BT solution, the operator was first prompted to obtain the preweighed sample bottles designated for the unspiked BT (UB) samples and to install a new, clean, disposable sampling assembly in the BT solution-sampling system. In addition, a new, clean, disposable, polyethylene sleeve was placed in the orifice of the gate-type access valve on the BT to prevent contamination of the valve's internal surfaces by droplets of solution that might adhere to the in-tank portion of the sampling line when the line was later removed from the tank. The operator was then prompted to start the BT mixer (the solution was stirred continuously during sampling) and obtain the appropriate number of samples, each about 25 mL.

After the samples were taken, OPRDSx prompted the operator to remove and discard (to waste) the sampling assembly and polyethylene sleeve and to cap and weigh the individual sample bottles. The bottle weighings were made in triplicate to the nearest 0.001 g. From the weighing data, the computer calculated a net solution weight for each sample, using the previously recorded tare for each sample bottle. Next, the BT assembly was automatically weighed as before. The net weight of solution in the BT was calculated and recorded as the weight of the unspiked, mixed, sampled (UMS) BT solution. The computer also calculated the weight of solution lost during sampling by comparing the UMU solution weight with the sum of the UMS solution weight and the net weights of solution in the several sample bottles. This lost solution, usually attributable to the small droplets of liquid that adhered to the inside of the tubing in the discarded sampling assembly, generally amounted to 2 g or less. All the information from these weighings and calculations was displayed for operator acceptance and, once accepted, logged. The program then proceeded to the next BT operation, spiking of the BT solution.

(2) Spiking of the Blend Tank Solution

The BT solution that contained each fuel-bearing segment was spiked in a manner that ensured verifiable transfer of the spike into the BT, complete spike dissolution, and thorough homogenization and isotopic equilibration of spike and segment uranium in the solution. The BT spiking operations were

automatically omitted from the DDS procedure for plenum dissolutions and blank runs because the uranium content of the BT solution was small in these cases and did not need to be determined with high precision and accuracy.

The spike added to the BT solution was an accurately weighed quantity of NBS Standard Sample 950a (a natural uranium assay standard in the form of U_3O_8), contained in a sealed nickel capsule. For QA purposes, the preparation, storage, and dispensing of the spikes followed strict guidelines. The spikes were prepared in batches by the ACL according to the procedure in Document C-0030-289 (Attachment 1) and were stored in labeled, closed glass bottles in a locked cabinet in one of the ACL laboratories. At the onset of DDS operations with segments from a given fuel rod, the group of spikes designated for use with that rod was transferred to the DDS task leader and stored in a safe in the DDS work area.

Each fuel-bearing segment to be dissolved in the DDS was assigned a particular spike by means of an entry in the FRIF. Two sizes of NBS 950a spike were used for the EOL campaign with the aim of keeping the spike/sample ratio for most segments within the optimum 1:5 to 5:1 range for subsequent mass spectrometric measurements on uranium in the spiked BT solution: one size contained a nominal weight of U_3O_8 equivalent to 1 g of uranium and the other, a nominal weight equivalent to 3 g of uranium. The 1-g spikes were used for segments having a uranium loading of less than 2.5 g, and the 3-g spikes were used for segments containing more than 2.5 g of uranium.

In executing the BT spiking operations, the OPRDSx program first retrieved, from the FRIF, the spike identification assigned to the segment being processed and directed the operator to obtain the spike from the shift supervisor and transfer it into the cell enclosure. Next, the operator was prompted to weigh the spike, including the bottle that held it, to verify the spike identity. The computer compared this spike weight with a corresponding weight recorded in a computer file at the time the spike was prepared by the ACL. If the weights agreed within preset limits, the program proceeded to the next step. Otherwise, the operator was required to resolve the discrepancy and repeat the weighing before the program would continue.

Once the spike identity was verified, the operator was prompted to charge the spike to the BT by gently "pouring" the nickel capsule into the (funnel-shaped) opening of the BT access valve. This method of addition of the spike avoided touching the spike capsule with possibly contaminated M/S manipulator fingers and thereby contaminating the BT solution with extraneous uranium. The operator verified that the spike had passed through the access valve and into the tank by visual inspection of the orifice, using a mirror positioned over the valve, and also verified that the BT balance had registered a weight increase upon addition of the spike.

Next, the BT mixer was started and a slow flow of cell air through the BT headspace was established by a procedure analogous to that described for mixing of the unspiked BT solution. The program next proceeded to a BT heatup sequence wherein the BT solution temperature, vacuum-reservoir pressure, BT pressure, and BT external temperature were read and displayed every 30 s. The computer also monitored the solution heatup rate and the rate of pressure increase in the vacuum reservoir and prompted the operator to make appropriate adjustments if these rates were outside preset tolerances.

The heatup sequence continued until the solution temperature reached 95°C, at which time the program initiated the "spike dissolution" routine. The start time of the spike dissolution was recorded, and the solution temperature was held between 95 and 105°C for 60 min. Monitoring of appropriate temperatures, pressures, and rates of change continued through the dissolution routine, and messages to the operator calling for appropriate adjustments of the heating rate or air flow were displayed as required. When 60 min at temperature had elapsed, the spike-dissolution end time was automatically logged, and the operator was prompted to turn off the BT heater and mixer and to place the BT assembly in the standard weighing condition.

The BT assembly was then weighed automatically as previously described; the net solution weight obtained from these weighings was recorded as the spiked, mixed, unsampled (SMU) BT solution weight. The SMU solution weight was then used, with the UMS weight determined previously, to calculate a value for any loss of weight during the spike dissolution. All of the weighing data was displayed for operator acceptance and logged. Weight loss during spiking of the BT generally amounted to a few (less than ten) grams and was attributable to evaporation of the hot solution. When the SMU weight data were accepted by the operator, the program proceeded to sampling of the spiked BT solution.

(3) Sampling of the Spiked Blend Tank Solution

To make efficient use of operator time during the BT operations, the spiked BT solution was not cooled prior to being sampled. Cooling the solution at this point in the procedure would have required connecting cables and fittings to the BT and then disconnecting them to regain the standard weighing condition. When performed with M/S manipulators, such operations are time-consuming. Sampling the solution while it was still warm entailed no significant disadvantages, although the solution weights obtained may not have been as reliable as if the solution were cooled first, because of larger vapor losses taking place. The weights of the spiked BT solution and solution samples are of operational interest only and are irrelevant to subsequent analytical calculations (see Section V.E); thus, they did not need to be determined as accurately as, for example, the corresponding data on the unspiked BT solution.

Four separate samples of the spiked BT solution were weighed by a procedure analogous to that followed during sampling of the unspiked BT solution. The net weight of solution in the BT after removal of the samples--designated the spiked, mixed, sampled (SMS) BT solution weight--was added by the computer to the sum of the net solution weights for the spiked BT solution samples and was automatically compared with the SMU solution weight to give a value for the solution lost during sampling the spiked BT. In general, this calculated weight loss (in the range 2 to 5 g) was somewhat larger than that found for sampling the unspiked BT, probably as a result of evaporation of the warm solution. All of the weight data obtained during the spiked BT sampling were displayed for operator acceptance and logged in appropriate computer and hardcopy files.

(4) Transfer of Blend Tank Solution to Waste Storage Tank

When the foregoing operations had been completed, OPRDSx prompted the operator to initiate cooling of the BT solution and then proceeded

to direct the operator through a series of post-dissolution operations (described in the next subsection) while the solution cooled. When the BT solution temperature reached 60°C or less, the operator was prompted to tilt the BT by means of the stanchion support mechanism and to implement transfer of the solution to the waste-storage tank designated in the FRIF for the given segment. This transfer was made by pumping the solution out of the BT through a portable plastic drain line inserted through the BT access valve. Tilting the BT while it was being drained resulted in the removal of all but a few grams of solution from the tank. Following computer prompts, the operator then rinsed the BT with 200 g of dilute nitric acid and transferred the rinse solution to the same waste tank. After the rinse solution was removed, the BT was automatically weighed, and the weight of solution remaining in the BT was calculated as the difference between this weight and the empty BT weight recorded at the beginning of the dissolution. If the remaining solution weight exceeded 20 g, the program automatically repeated the prompts that directed draining of the tank. This requirement was included in the procedure because large amounts of fuel-bearing solution left in the BT at this point hampered the effectiveness of subsequent BT decontamination procedures. During these operations, the computer monitored and recorded readings from the waste-tank level probes, as well as documented the weighing data and other pertinent information such as reagent batch number and weight of the rinse reagent. The empty, but still contaminated, BT was set aside for later decontamination [Section IV.E.3.f.(1)] at a convenient time in the DDS operations schedule.

e. Post-Dissolution Operations

Following completion of the BT operations in each dissolver run, the operator was prompted through a series of operations to restore the equipment and work areas to a condition appropriate for beginning the next run. These operations are listed below, with a brief description of the purpose of each.

(1) Flushing the Off-Gas Hold Tank

The off-gas hold tank was flushed with air (30 min at a flow rate of 5 to 10 L/min) to displace off-gas components from the run just completed.

(2) Inventory of Undissolved Cladding Hulls

To cross-check the identity of the segment charged to the dissolver and to obtain information regarding the extent of dissolution of the segment cladding, we made an inventory of the undissolved cladding hulls, as follows. The dissolver vessel was opened, the fuel basket was removed, and the cladding hulls remaining in the basket were individually inspected and counted and then weighed as a group. The computer compared the hull count with the number of hulls that would be expected, based on the number of cuts made in shearing the segment. A recount was done if the numbers disagreed. If the discrepancy persisted, the operator was required to enter any observations made during the counting. The DDS operators counted only hulls that were recovered intact and did not attempt to piece together hulls that might have been recovered as fragments. In general, discrepancies between the number of hulls expected and recovered were explained by the presence of cladding fragments among the hulls.

The OPRDSx program calculated an estimate of the weight of cladding that had dissolved, using the measured hull weight and the cladding-weight estimate, as found in the FRIF, for the appropriate segment.

(3) Removal of the Filter-Housing Assembly

The filter-housing assembly was removed from the solution-transfer system, and its end-fittings were capped to avoid spreading residual solution while the housing was being transferred to the in-cell maintenance area. The assembly was subsequently decontaminated and disposable components were replaced to prepare it for reuse in the dissolver system.

(4) Treatment of Discarded Sampling Assemblies

Discarded sampling assemblies were rinsed with distilled water to reduce residual levels of radioactivity and were cut into small pieces to reduce the volume they occupied in the waste containers that would be transferred out of the cell. This treatment reduced radiation levels at the surface of the containers and increased the payload, which in turn reduced disposal cost.

The rinse solution was concentrated by evaporation in a heated vessel; periodically, the concentrate was added to the liquid-waste storage tanks for disposal with other liquid residues from the DDS operations.

(5) Check for Liquid in the Off-Gas Hold Tank

A sampling bottle was placed under the drain line for the off-gas hold tank, and the drain was opened to check for liquid that might have accumulated in the off-gas system. Such liquid could arise from solution droplets entrained with the dissolver off-gas or from vapor that condensed in the tank. This check was performed routinely in the early portion of the EOL campaign, but was discontinued after processing of segments from several rods showed that no liquid accumulated in the hold tank under normal conditions. It was reinstated as a routine operation after a mishap with a later segment (J-03) showed that, under certain conditions, dissolver solution could be carried into the off-gas system without the operator being aware of it. If liquid was found in the off-gas hold tank, it was submitted for analysis, and appropriate actions were taken to recover any fuel material associated with it to account for this fuel in the segment assays.

(6) General Housekeeping

General housekeeping was performed to ensure that all work-area tools were returned to their designated storage locations, and that the work area was clean and free of unnecessary clutter. As part of this effort, the stainless-steel drip pan under the dissolver control-valve bank was rinsed with dilute nitric acid and wiped down to minimize accumulation of fuel material on the tray surfaces. Because of this cleaning after each dissolver run, solution that collected in the tray from leaking valves or transfer lines could be recovered without fear of gross contamination of the recovered solution by extraneous fuel material from previous runs. Such leakage occurred on several occasions during the EOL campaign but was successfully dealt with in every case (see Section V.C.3.b), partially due to the good housekeeping practiced in the cell work areas.

f. Decontamination of Reusable Dissolver Components

Wherever practical, small equipment items used in analytically sensitive operations (e.g., sample bottles, sampling lines) were used once and discarded to prevent cross-contamination of fuel material or samples from one segment with those from another. However, economic considerations required that individual components be decontaminated and reused for three kinds of items: the BTs, the filter housings for the solution transfer system, and the gas-sampling cylinders. This section outlines the decontamination procedures employed for each type of item.

(1) Blend-Tank Decontamination

Special care was taken to remove residual fuel solution from each BT between uses and to ensure that the tank was thoroughly dry before reuse. These precautions were necessary to prevent contamination of the BT solution from one segment with fuel from another and to ensure a valid net weight for the solution collected in the BT during a given segment dissolution. (If liquid is present in the "empty" BT when its tare weight is determined, the net weight of solution in the tank, as determined by subtracting the tare from a subsequent assembly weight, will be lower than the actual solution weight by the amount of this extraneous liquid.)

To achieve these conditions, each BT was taken through a decontamination procedure that included two separate refluxes of dilute nitric acid in the tank and a drying step wherein the tank was heated while being flushed with a stream of air to displace vapor in the tank. The decontamination procedure was carried out under control of a subsection of the OPRDSx program. This subsection could be initiated as part of the post-dissolution operations that immediately followed dissolution of a given segment or could be run separately at a later time. If run separately, the procedure was treated as a continuation of the OPRDSx run for the segment dissolution for which the BT was last used. Thus, records related to the BT decontamination were kept together with records of other data from that segment dissolution.

For each reflux rinse of the BT, 250 mL of dilute nitric acid was charged to the tank, heated to 95°C, cooled to 70°C, and removed by means of the BT sampling system (with clean, new sampling assemblies sized to fit appropriate sample bottles). The first rinse solution was discarded to the waste-evaporation vessel, while the second one was collected in a new, clean sample bottle and submitted for analysis. The BT was dried by heating to an internal temperature of 120°C under a controlled air flow for 30 min. The dried BT was cooled, weighed, and placed in storage pending the results of analysis of the second rinse solution. The dry BT weight was automatically compared with the empty BT weight recorded at the beginning of the dissolver operations. The weight after decontamination had to be less than the recorded empty weight plus 2 g or the OPRDSx program directed the operator to repeat the drying step or take other remedial action as appropriate. If the dry BT weight was acceptable, the weight was logged in the segment dissolution data records and in the HISLOG file for the BT.

The second reflux rinse solution was analyzed for total uranium as described in Section IV.F.1. For decontamination of the BT to be judged satisfactory, uranium in the rinse solution had to fall below 100 μg, a

value that pre-EOL testing had shown to correspond to a residual level of 10 μg or less uranium in the BT. This quantity of residual uranium, in turn, corresponded to an amount of fuel in the BT that would have a negligible impact on the composition of fuels from other segments subsequently collected in the BT. The results of analysis of the individual BT rinses were reported by the ACL to the DDS supervisor, who entered them into the HISLOG files for each BT. If the results indicated satisfactory decontamination, the supervisor also entered a code indicating approval for reuse of the tank.

(2) Decontamination of Filter-Housing Assemblies

In spite of the difficulty associated with handling small parts with M/S manipulators, filter-housing assemblies that became contaminated during dissolver operations had to be decontaminated remotely because of a buildup of ^{125}Sb, ^{95}Nb, and other easily hydrolyzable, gamma-emitting nuclides on the internal metal surfaces of the housings. The mechanism for this buildup has not been identified, but testing early in the EOL campaign indicated that the radioactivity on the metal surfaces could not be removed without drastic chemical cleaning, sufficient to etch the surfaces.

Each contaminated housing was disassembled at the general-purpose work area of the DDS cell. Special jigs and wrenches fabricated for this purpose were used. The prefilter and membrane filter from each unit was removed and placed in a labeled, covered plastic Petri dish, and the radioactivity of the filter media was measured with the portable in-cell radiation probe. Individual filters generally read between 20 and 100 R/h at 4 in. On the basis of gamma-counting data obtained for some of the more-active specimens, activity on the filters was due primarily to ^{125}Sb, with lesser contributions from ^{95}Nb, and only minor contributions from the fission products that were of interest in our work (i.e., ^{137}Cs and ^{144}Ce). The individual sets of filter media were stored in a shielded container within the cell and were disposed of at the end of the campaign by incorporating them into the cement that contained the liquid dissolver residues.

The metal housing of each filter assembly was visually inspected for the presence of undissolved fuel particles (none was ever found during the campaign) and thoroughly rinsed with dilute nitric acid. The rinse solutions were collected and their volume reduced in the waste-evaporation vessel for periodic addition to the waste-storage tanks.

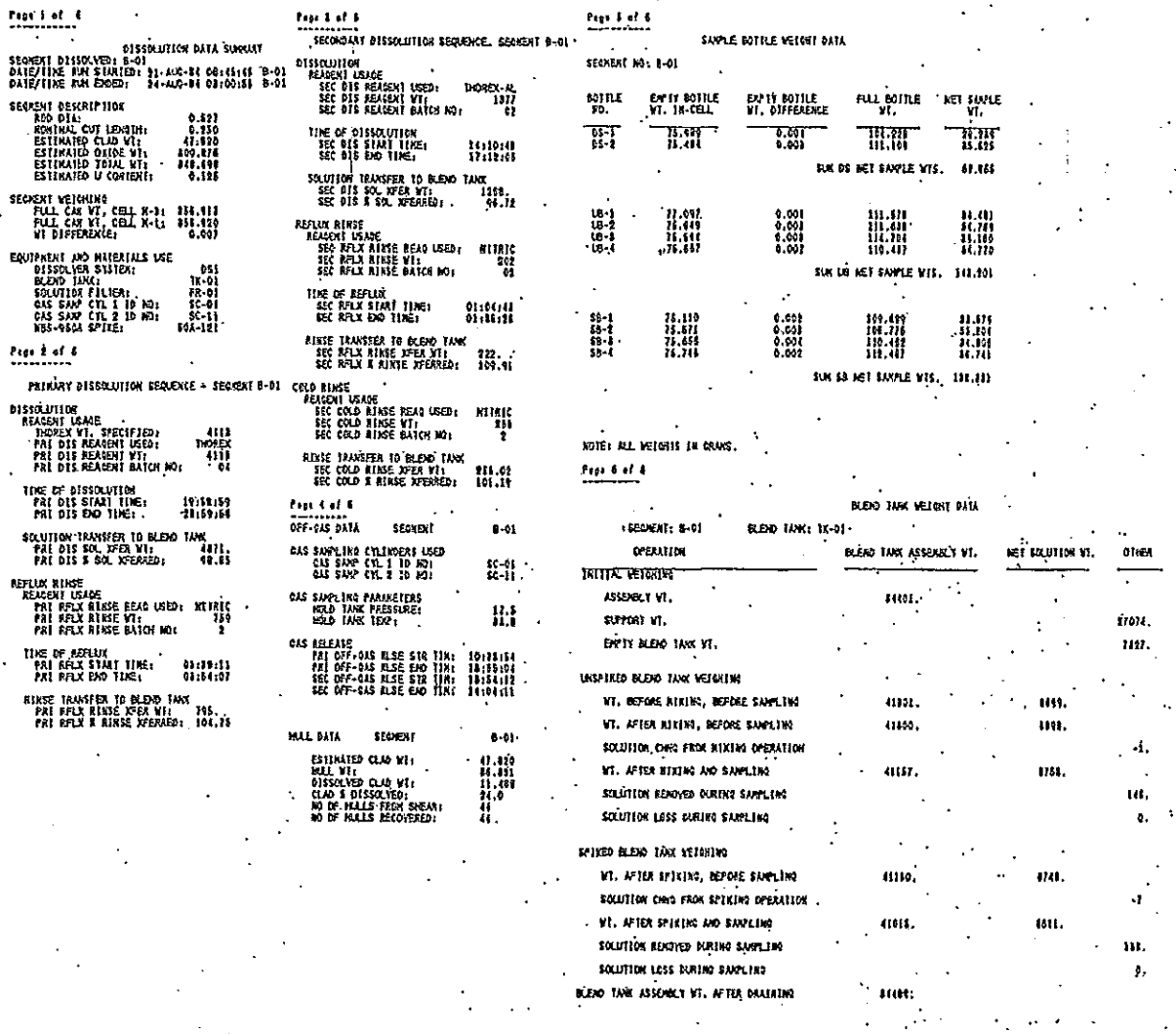
Next, clean, new filter media and O-rings were installed in each housing, and the unit was then reassembled. Each assembly was then pressure-tested by attaching it to the pressure manifold installed at the work station for this purpose and pressurizing the manifold to 120 psig. To pass the test, the assembly had to lose no more than 1 psig over a 1-min period. When an assembly was judged satisfactory, it was removed from the manifold, its ends were capped, and it was placed in a storage area designated for decontaminated filter-housing assemblies. The operator entered into the HISLOG file for each assembly the information pertinent to the decontamination, including the radiation-monitor reading obtained for the used filter media.

(3) Purging of Gas-Sampling Cylinders

After the gas in each sampling cylinder had been analyzed, the cylinders were returned from the ACL to the DDS and connected to the off-gas sampling station. Each cylinder was then purged of residual sample gas by flushing with compressed air for 5 min. After the purging operation, the operator entered the date of purging and his or her identity into the HISLOG files for the appropriate cylinders. The cylinders were then ready for reuse.

4. Data Summary and Management Review of Segment Dissolution

After DDS operations for any given segment, the data were processed with a stand-alone report-generation program, which produced a dissolution data summary as illustrated in Fig. 17. This program read the FRIF for the rod from which the segment was sheared and the summary data file generated during DDS operations with the segment, calculated results from the various measured



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DISSOLUTION DATA SUMMARY

SEGMENT DISSOLVED: B-01
DATE/TIME RUN STARTED: 31-AUG-84 08:55:55 B-01
DATE/TIME RUN ENDED: 04-AUG-84 03:00:58 B-01

SEGMENT DESCRIPTION
ROD DIA: 0.829
NOMINAL CUT LENGTH: 0.950
ESTIMATED CLAD WT: 47.920
ESTIMATED OXIDE WT: 809.876
ESTIMATED TOTAL WT: 848.698
ESTIMATED U CONTENT: 0.826

SEGMENT WEIGHING
FULL CAN WT, CELL N-1: 856.913
FULL CAN WT, CELL N-1: 856.920
WT DIFFERENCE: 0.007

EQUIPMENT AND MATERIALS USE
DISSOLVER SYSTEM: DSS
BLEND TANK: TK-01
SOLUTION FILTER: FR-01
GAS SAMP CYL 1 ID NO: SC-01
GAS SAMP CYL 2 ID NO: SC-11
NBS-960A SPIKE: 960A-121

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PRIMARY DISSOLUTION SEQUENCE - SEGMENT B-01

DISSOLUTION
REAGENT USAGE
THOREX WT. SPECIFIED: 4118
PRI DIS REAGENT USED: THOREX
PRI DIS REAGENT WT: 4118
PRI DIS REAGENT BATCH NO: 04

TIME OF DISSOLUTION
PRI DIS START TIME: 19:58:59
PRI DIS END TIME: 28:59:08

SOLUTION TRANSFER TO BLEND TANK
PRI DIS SOL XFER WT: 4071.
PRI DIS S SOL XFERED: 98.85

REFLUX RINSE
REAGENT USAGE
PRI RFLX RINSE REAG USED: NITRIC
PRI RFLX RINSE WT: 759
PRI RFLX RINSE BATCH NO: 2

TIME OF REFLUX
PRI RFLX START TIME: 03:09:11
PRI RFLX END TIME: 03:04:07

RINSE TRANSFER TO BLEND TANK
PRI RFLX RINSE XFER WT: 795.
PRI RFLX R RINSE XFERED: 104.75

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SECONDARY DISSOLUTION SEQUENCE, SEGMENT B-01

DISSOLUTION
REAGENT USAGE
SEC DIS REAGENT USED: THOREX-AL
SEC DIS REAGENT WT: 1977
SEC DIS REAGENT BATCH NO: 02

TIME OF DISSOLUTION
SEC DIS START TIME: 14:10:48
SEC DIS END TIME: 17:12:05

SOLUTION TRANSFER TO BLEND TANK
SEC DIS SOL XFER WT: 1359.
SEC DIS R SOL XFERRED: 96.72

REFLUX RINSE
REAGENT USAGE
SEC RFLX RINSE REAG USED: NITRIC
SEC RFLX RINSE WT: 202
SEC RFLX RINSE BATCH NO: 01

TIME OF REFLUX
SEC RFLX START TIME: 01:04:48
SEC RFLX END TIME: 01:06:38

RINSE TRANSFER TO BLEND TANK
SEC RFLX RINSE XFER WT: 222.
SEC RFLX R RINSE XFERRED: 109.91

COLD RINSE
REAGENT USAGE
SEC COLD RINSE REAG USED: NITRIC
SEC COLD RINSE WT: 250
SEC COLD RINSE BATCH NO: 2

RINSE TRANSFER TO BLEND TANK
SEC COLD RINSE XFER WT: 824.02
SEC COLD R RINSE XFERRED: 101.19

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OFF-GAS DATA SEGMENT B-01

GAS SAMPLING CYLINDERS USED
GAS SAMP CYL 1 ID NO: SC-01
GAS SAMP CYL 2 ID NO: SC-11

GAS SAMPLING PARAMETERS
HOLD TANK PRESSURE: 12.5
HOLD TANK TEMP: 81.0

GAS RELEASE
PRI OFF-GAS RLSE STR TIM: 10:08:54
PRI OFF-GAS RLSE END TIM: 10:55:04
SEC OFF-GAS RLSE STR TIM: 10:54:12
SEC OFF-GAS RLSE END TIM: 11:04:11

HULL DATA SEGMENT B-01

ESTIMATED CLAD WT: 47.920
HULL WT: 86.851
DISSOLVED CLAD WT: 11.498
CLAD % DISSOLVED: 24.0
NO OF HULLS FROM SHEAR: 46
NO OF HULLS RECOVERED: 46

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SAMPLE BOTTLE WEIGHT DATA

SEGMENT NO: B-01

BOTTLE NO.	EMPTY BOTTLE WT. IN-CELL	EMPTY BOTTLE WT. DIFFERENCE	FULL BOTTLE WT.	NET SAMPLE WT.
DS-1	25.499	0.001	101.228	80.916
DS-2	25.484	0.003	111.109	85.625
			SUM DS NET SAMPLE WTS.	68.866
LB-1	27.097	0.001	111.878	84.481
LB-2	26.649	0.003	111.638	84.789
LB-3	26.644	0.003	114.784	88.140
LB-4	26.697	0.002	110.467	84.770
			SUM LB NET SAMPLE WTS.	342.801
SB-1	26.110	0.003	109.499	83.376
SB-2	25.871	0.003	108.726	82.854
SB-3	25.655	0.004	110.492	84.836
SB-4	26.746	0.002	110.487	83.741
			SUM SB NET SAMPLE WTS.	334.803

NOTE: ALL WEIGHTS IN GRAMS.

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BLEND TANK WEIGHT DATA

SEGMENT: B-01 BLEND TANK: TK-01

OPERATION	BLEND TANK ASSEMBLY WT.	NET SOLUTION WT.	OTHER
INITIAL WEIGHING			
ASSEMBLY WT.	84101.		
SUPPORT WT.			87074.
EMPTY BLEND TANK WT.			7027.
UNSPIKED BLEND TANK WEIGHING			
WT. BEFORE MIXING, BEFORE SAMPLING	41831.	8859.	
WT. AFTER MIXING, BEFORE SAMPLING	41650.	8868.	
SOLUTION CHG FROM MIXING OPERATION			-1.
WT. AFTER MIXING AND SAMPLING	41557.	8758.	
SOLUTION REMOVED DURING SAMPLING			148.
SOLUTION LOSS DURING SAMPLING			0.
SPIKED BLEND TANK WEIGHING			
WT. AFTER SPIKING, BEFORE SAMPLING	41150.	8748.	
SOLUTION CHG FROM SPIKING OPERATION			-7
WT. AFTER SPIKING AND SAMPLING	41015.	8611.	
SOLUTION REMOVED DURING SAMPLING			138.
SOLUTION LOSS DURING SAMPLING			0.
BLEND TANK ASSEMBLY WT. AFTER DRAINING	84486.		

Fig. 17: Example of Dissolution Data Summary Report

parameters, and wrote the results to a new file in a format appropriate for management review. As Fig. 17 shows, the summary has seven major parts: (1) data that characterize the segment and codes that identify equipment and materials used in dissolution, (2) data pertinent to the primary dissolution sequence, (3) a similar listing for the secondary dissolution, (4) data related to the off-gas sampling operations, (5) data regarding the recovered cladding hulls and extent of cladding dissolution, (6) sample bottle weights, and (7) weights obtained during BT operations. The items included in each section of the summary are self-explanatory and will therefore not be discussed individually.

The dissolution data summary for each segment was reviewed by the DDS task leader, the project principal analyst, and the project manager to ensure completeness of the data listings and to identify any operational or processing deviations that might have been indicated by the data. Omissions or inconsistencies were dealt with on a case-by-case basis. In general, missing data were retrieved by the DDS task leader from the hardcopy process log or from the manual logbook maintained at each dissolver work station, and were added to the dissolver data summary file by means of a special data-entry program. This program not only wrote the new information to the summary file, but also noted in the file that it had been edited, and indicated the identity of the editor and the date. If the new data replaced previous entries that were judged to be in error during the post-dissolution review, both the old and new information were retained in the summary data file, although the program that formatted the data to produce the dissolution data summary used only the most-recent entry in producing the report. This system for reviewing data from the segment dissolutions provided needed flexibility in the handling of the computerized data records and, at the same time, maintained strict traceability of the recorded information for QA purposes.

5. Archive Storage of Solution Samples

To satisfy the project requirement for taking and retaining samples of fuel solution for each segment, half of the samples of each solution type [i.e., secondary dissolution (DS), unspiked BT (UB), and spiked BT (SB)] were placed in archive storage, while the other half were transferred from the DDS to the Analytical Hot Cell for chemical and radiometric analysis. Specific samples of each type were designated for each purpose. From the two DS samples obtained for fuel-bearing segments, the first (the DS-1) sample was archived, and the second (the DS-2) was submitted for analysis. We reasoned that the DS-2 sample was less prone to contamination, since taking of the DS-1 sample rinsed the solution transfer-system sampling port, and would provide a more-representative primary analysis of the secondary dissolution. Among the four samples obtained from each type of BT solution, the first and last (i.e., UB-1 and UB-4 or SB-1 and SB-4) were analyzed and the middle two (i.e., UB-2 and UB-3 or SB-2 and SB-3) were archived. Duplicate samples of each BT solution were analyzed to assess sampling errors arising from inhomogeneity of the BT solution. Because the BT solution was continuously mixed during sampling, we expected that such inhomogeneity would have its greatest impact on a comparison between the first and last samples taken. These were, therefore, the samples we selected for immediate analysis. Moreover, the pair of archives samples and pair of analytical samples selected in this way were both symmetrically taken about the midpoint of the sampling operations and shared a common average sampling time with the entire group of four samples. As a consequence, the average of

each analytical result obtained for one pair was expected to be comparable to that of the other pair and to that of the whole group.

To aid the DDS operators in selecting individual samples for transfer to storage or to the Analytical Hot Cell, different-colored labels were used for the bottles. Labels on the archives samples were yellow, the other white.

The archives samples were placed in special bottle holders inside sealable SS cans of the type used with the can-out intercell transfer system. Each can held 12 bottles, and when full, it was transferred to one of the shielded storage tubes located in the floor of the corridor adjacent to the DDS cell. Detailed records were kept with regard to the identity of the bottles in each can and the location of each can in the storage tubes so that individual bottles could be readily retrieved if required. Approximately 800 bottles containing archives solution samples were accumulated during the EOL campaign.

F. Analytical Operations

Operations performed by the ACL on behalf of the LWBR-POB project included (1) preparation of reagents and standards for the DDS operations and (2) analysis of solution and gas samples from operations in the FSSF and DDS. Each step in these analytical operations was performed in accord with a written or computerized procedure that guided a qualified analyst through appropriate preparative chemistry or measurement methodology. A listing of the written procedures employed in these operations is presented in Attachment 1.

Preparation of reagents (Thorex, Thorex-Al, and dilute nitric acid rinse) for use in the DDS was described in Section IV.E.3.b., and the NBS 950a spikes prepared for addition to the dissolver blend-tank solutions were described in Section IV.E.3.d.2. In the following sections, we summarize the procedures that were employed in analyzing the dissolver-solution samples and briefly describe the analysis of gas samples by mass spectrometry.

1. Chemical and Radiometric Analysis of Dissolver Solutions

a. Overview

Selected solution samples obtained during dissolution of each segment were transferred from the dissolver cell to the Analytical Hot Cell by means of the radio-controlled MULE. When the set of samples from a given segment was transferred, a computer file, designated the DDS information file or DDSIF, was automatically generated in the project computer system. This file summarized data pertinent to each solution sample as recorded during the segment dissolution, including (1) the full and empty weights of each sample bottle (samples submitted for analysis as well as those placed in archive storage were listed), (2) the weight of solution contained in the unspiked blend tank (UBT) for the specified segment, and (3) estimates of the total oxide weight and total uranium loading of the dissolved segment as provided by BAPL in the shearing plan for the corresponding fuel rod. The data in the DDSIF were used by computer programs that controlled subsequent aliquoting and analysis of the samples to perform such tasks as verifying the identity of the samples, applying

corrections for evaporation of the solutions, and specifying optimum aliquot sizes for the analysts to take for each designated analysis.

For every fuel-bearing segment, the samples received for analysis included one sample of the secondary dissolver (DS) solution, two separate samples of the UBT solution, and two separate samples of the spiked blend tank (SBT) solution (cf. Section IV.E.5). A weighed aliquot of the DS sample was spiked with NBS 993 (primarily ^{235}U) and was analyzed to determine its $^{233}U/^{235}U$ ratio for use in computing, by isotope dilution formulas, the concentration of segment uranium in the DS solution. Each of the two UBT samples was divided by weight into four aliquots to separately measure (1) the segment uranium isotopy, (2) the uranium concentration in the UBT solution, (3) the concentrations of the fission products ^{137}Cs and ^{144}Ce, and (4) the concentration of the fission product ^{95}Zr. One aliquot from each of the SBT samples was prepared to determine the $^{233}U/^{238}U$ isotope ratio in the SBT solution and thereby allow calculation of the amount of segment uranium present in the SBT. Our approach of taking a single aliquot from each of two separate samples of the BT solutions provided replicate data with which we could evaluate the reproducibility of the entire sampling, sample preparation, and measurement sequence. These data are used in Appendices B, D, and E to assess the quality of such operations as mixing of the BT solution, as well as to obtain a measure of random errors associated with the results of the individual assays that were performed on the dissolved segments.

In contrast to the fuel-bearing segments, only two dissolver solution samples were analyzed from dissolution of each fuel rod plenum section. These were duplicate samples of the UBT solution (the BT was not spiked during plenum dissolutions), which were assayed for the ^{233}U and ^{232}Th concentration by mass spectrometric isotope dilution (MSID). In general, uranium in the dissolved plenums was at such low levels as to preclude meaningful measurement of its isotopy. On a few occasions, however, uranium in a specific rod plenum was at a level (concentration in the UBT solution greater than 10 $\mu g/g$) that allowed its isotopy to be determined. In these cases, an additional aliquot from each UBT sample was taken (subsequent to obtaining the assay results) and prepared for isotopic analysis.

During dissolution of a few segments, there were mishaps (see Section V.C.3.b) which resulted in additional samples being generated as part of actions taken to recover. When these special samples took the form of solutions, they were treated in a manner similar to the UBT solutions. Often, however, the samples were submitted as tissues used in wiping down specific areas of the dissolver equipment or hot cell. These tissues were thoroughly leached with nitric acid, and the leach solutions were treated in the same way as were the other special samples.

Each solution aliquot designated for a particular type of measurement or analysis was prepared in a manner to provide a suitable sample. In cases where uranium isotope ratios were to be measured (the case for both uranium isotopic measurements and assays), uranium in the aliquot was isolated and purified for subsequent mass spectrometric or alpha pulse height analysis (APHA). Aliquots designated for fission-product assays by gamma spectrometry were diluted to a uniform volume consistent with the geometry requirements of the counting techniques that were employed.

Lakes, Melvin E (Mel)

From: Graczyk, Donald G. [graczyk@anl.gov]
Sent: Monday, May 05, 2008 12:53 PM
To: Dalton, David
Cc: Leonard, Ralph A.; Regalbuto, Monica C.; Bowers, Delbert L.; Emery, Jeffrey W.; Sullivan, Vivian S.; Rock, Cynthia M.
Subject: RE: Data from Analysis of Shippingport Fuel
Attachments: Inconel X Technical Data.pdf; Cr in Cement Calc 5-4-08.xls; Bettis Info on Hardware.pdf; ANL-87-2 Partial Report.pdf

Hello David:

Sorry it took me a while to get a response to you on your questions regarding the LWBR-POB waste you are interested in.

As background, I am attaching a .pdf file with selected pages from the final project report, ANL-87-2, which gives an overview of operations.
Waste Treatment is covered on pp. 40 thru 44. Note there is a reference to hulls having been cemented separately from the dissolver solutions to produce non-TRU waste. This clarifies my vague recollection that the hulls were cemented, but removes any possibility that the hulls were included with the dissolver solution wastes you are interested in. The dissolver operations are covered in pp. 89 thru 109.

In answer to your questions: Unfortunately, I am certain that no analysis was done on the dissolver-solution waste to determine trace element content (and in particular, the concentrations of Cr, Cd, or Pb) and am not aware of any calculations to estimate them. Nevertheless, I can share some information that might help make an evaluation possible.

First: with regard to your request for info on the dissolution and solidification processes, see the ANL-87-2 file -- it has sections on the dissolution and cementation operations that should be helpful. The report notes that the cladding hulls were recovered, counted, and weighed for each segment dissolved.

Second, I gathered some information from various sources that could provide a bounding case evaluation. Argonne dissolved 17 fuel rods in the course of its EOL campaign, including five seed rods, 4 standard blanket rods, six power-flattening blanket rods, and two reflector rods.
Each rod contained zircaloy-4 cladding and plenum hardware (spring) made of the NiCrFe alloy Inconel X. We have talked about the zircaloy and agreed that it can be assigned a nominal Cr content of 0.1 wt%, with only trace impurity levels of Cd and Pb. I am not aware of any constituents of the rods that would contribute substantive amounts of Cd or Pb to the waste (I don't expect fission product Cd to be significant for U-233). Thus, the pertinent question is whether the waste is hazardous by virtue of its Cr content. From a Bettis table of info on fuel rod hardware, a mass of zircaloy and NiCrFe alloy in each rod type is available (see Bettis info .pdf). If one assumes the Inconel X is 17%Cr (Max in spec), and the zircaloy is 0.1wt%, then total Cr from all the dissolved rods is on the order of 286 g, mostly from the Inconel (only 11 g from all the zircaloy)--see the attached Excel spreadsheet.

For a bounding calculation, let's assume all of the hardware dissolved.
This ended up in 700 L of waste solution that was cemented in approximately 233 cans, each containing 1.5 gallons of product cement.
The maximum concentration of Cr in the solution is thus 286 g Cr/700 L solution or 409 mg Cr/L. Each can held about 3 L solution, or 1226 mg Cr at most. Assuming a density of 2 for the cement (you might be able to make a better estimate from data you have on the waste packages) I estimate the weight of cement in a can at 1.5 gal x 3.785 L/gal x 2 kg cement/L =

11.4 kg. Thus, the maximum Cr content of the cemented waste is on the order of 1226 mg/11.4 kg = 108 mg/kg. If one put this material through a TCLP extraction (100 g to 2000 mL extraction fluid) and all of the Cr extracted, the TCLP result would be 5.4 mg Cr/L, which is greater than the TCLP regulatory limit of 5 mg/L for Cr and leads to the conclusion that the waste could be hazardous by virtue of its Cr content.

To refine the estimate a bit, I looked up the data for dissolutions of the plenum segments of the 17 rods processed at ANL. The plenum section of the rods contained the Inconel springs and no fuel. Thus, looking at the weight of the sheared plenum segment and the weight of "hulls"
recovered after dissolution, one can estimate how much of the Inconel hardware might actually have dissolved. The data are in the second worksheet of the Excel file attached. It looks like a large fraction of the Inconel was dissolved in every case since the mass that dissolved tracks the inconel mass fairly well for all rod types(note that for Rod P, I had to estimate the amount because the listed mass of hulls exceeded the segment mass -- something in error). This refinement gives a projected TCLP maximum concentration of about 4.6 mg Cr/L. I would say this is still too close to call and would hesitate to conclude the waste can't be hazardous. One might be able to refine the estimate a bit further if a better value for the density of the concrete were available. I used the value 2g/cc, but a typical cement density could be justified to be 2.3 g/cc. This would lower the maximum Cr level to 2/2.3 x 4.6 = 4.0 mg/L (TCLP). As I mentioned above, you might have data from the waste packages that could help establish a density value.

Putting everything together, I would say one could make a good case that Pb and Cd are not of concern, and that Cr is the constituent of concern in evaluating whether these wastes are hazardous. The predominant source of Cr is the NiCrFe alloy (Inconel x) components in the fuel rods, which correspond mostly to the springs in the plenum sections. These components do appear to have dissolved to a large extent during the destructive analysis operations. The quantities of Cr associated with these components are of a magnitude that is in the neighborhood of the TCLP regulatory limit. Reasonable conservative assumptions project that the Cr is just below the threshold at which the waste could be hazardous. Whether one can justify not sampling on this basis, I can't say.

Hope this helps some.

Feel free to call if you have questions.

Don Graczyk
630-252-3489

-----Original Message-----
From: David Dalton [mailto:David_Dalton@RL.gov]
Sent: Tuesday, April 29, 2008 5:42 PM
To: Graczyk, Donald G.
Subject: Data from Analysis of Shippingport Fuel

Dear Mr. Graczyk,

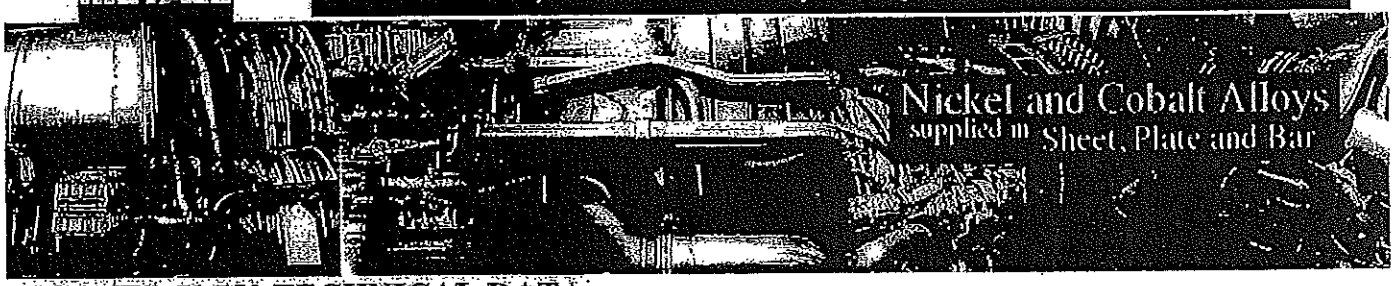
My name is Dave Dalton. I work for Fluor Government Group at the Hanford site. I deal with a lot of the difficult waste streams that Hanford has to treat and/or dispose of. One of the waste streams that I am working on is the U-233/Th-232 fuel that came from the Shippingport Reactor as part of the LWBR Proof-of-Breeding program. As you may recall, some of the fuel from this reactor was sent to Argonne for dissolution with acid and then the resulting solution was analyzed. The remaining solution was then neutralized with lime and solidified with cement.

Hanford has arbitrarily designated the waste as hazardous because of the Cr, Cd, and Pb in the cladding. This decision was not based upon actual data, but done to be conservative. (My comment to the people who decided to do this was that it may have been conservative from their point of view sitting behind their desk, but it certaintly wasn't conservative from an ALARA point of view to the people they concemmed to have to sample the waste by just deciding to call it hazardous.) In order to correct, if possible, this hazardous designation, I am trying to get information on the actual concentration of the Cr, Pb, and Cd in the solution (i.e., after fuel dissolution or in the solidified mass after adding cement. If I cannot find this data, I will try to do a mass balance to determine the concentration based upon computational results.

I am contacting you because I found a document that mention you sent some of the analytical results to INL for calculations to be performed.
Can you help me in any way with this task? Do you know of any analytical results or calculations to determined the Cd, Pb, and Cr in the dissolved fuel solution or the concrete? If not, do you know how I can get the recipe that was followed to do the dissolution and the solidification? I can be reached at 509-373-0188.

Thanks,
Dave Dalton

This message was sent by a visitor using the Argonne Employee Directory contact form at http://www.anl.gov/directory/.



INCONEL X-750 TECHNICAL DATA

Type Analysis | Description | Corrosion Resistance | Physical Properties
Heat Treatment | Workability | Typical Mechanical Properties

Type Analysis

Element	Min	Max
Carbon	--	0.08
Manganese	--	0.30
Silicon	--	0.50
Sulfur	--	0.01
Nickel + Cobalt	70.0 min	
Chromium	14.0	17.0
Iron	5.00	9.00
Aluminum	0.40	1.00
Titanium	2.25	2.70
Copper	--	0.50
Cb + Ta	0.70	1.20

Description

Alloy X-750 is a precipitation-hardenable alloy which has been used in applications such as high temperature structural members for gas turbines, jet engine parts, nuclear power plant applications, heat-treating fixtures, forming tools, and extrusion dies. The alloy is highly resistant to chemical corrosion and oxidation and has high stress-rupture strength and low creep rates under high stresses at temperatures up to 1500°F (816°C) after suitable heat treatment.

Corrosion Resistance

Alloy X-750 has excellent resistance to chloride ion stress-corrosion cracking. It exhibits satisfactory resistance to numerous oxidizing environments. The alloy has similar corrosion resistance to alloy 600 in many media.

Physical Properties

Density
lb/cu in..... 0.300
kg/cu m..... 8303
Melting Range
°F..... 2540/2600
°C.....1393/1427

Thermal Conductivity

Temperature		Btu-in/ft²-hr-°F	W/m-K
°F	°C		
300	149	117	16.9
600	316	142	20.5
1000	538	184	26.5
1200	649	199	28.7
1400	760	218	31.4
1600	871	245	35.3

Electrical Resistivity

Condition	ohm-cir mil/ft	microhm-mm
	At Room Temperature	
Hot Rolled	764	1270
Solution Treated	716	1190
Solution Treated and Aged	746	1240

Modulus of Elasticity

Temperature		psi x 10(6)	MPa x 10(6)
°F	°C		
80	26.7	31.0	213.7
500	260.0	28.7	197.9
1000	538.0	25.0	172.4
1350	732.0	21.0	144.8
1500	816.0	18.5	127.6

Coefficient of Thermal Expansion

Temperature Range		10(-6)/°F	10(-6)/°C
80°F to	26.7°C to		
200	93	6.7	12.1
600	316	7.5	13.5
1000	538	7.9	14.2
1200	649	8.1	14.6
1600	871	9.0	16.2

Specific Heat	Btu/lb-°F	kJ/kg-K
77/212°F (25/100°C)	0.10-0.11	0.42-0.46
77/1650°F (25/899°C)	0.13	0.54

Heat Treatment

Alloy X-750 is austenitic under all conditions. The alloy is heat treated by several different methods depending upon the application or requirement. Two common treatments are:
1. For maximum creep, relaxtion and rupture strength at temperatures above 1100°F (593°C):
Solution Treatment - 2100°F (1149°C), 2 to 4 hrs, air cool.
Intermediate Age - 1550°F (843°C), 24 hrs, air cool.
Final Age -1300°F (704°C), 20 hrs, air cool.
2. For highest room temperature yield strength and tensile ductility:
Stress Equaliztation - 1625°F (885°C), 24 hrs, air cool.
Precipitation Age - 1300°F (704°C), 20 hrs, air cool.

Workability

The furnace temperature should be 2100°F (1149°C)-for optimal starting temperatures of 1950/2000°F. For service below 1100°F (593°C), higher strength can be obtained by combining some cold work with heat treatment because the effects are additive.

Machinability
Alloy X-750 work hardens quickly and is more difficult to machine than most standard ferritic and martensitic alloys. The alloy is most easily machined in the stress-equalized

condition. Because specific cutting forces are high, the machine tools used must have ample power and the cutting speed should be slow. The tools must have smooth finishes, be sharp, and be very rigid. To avoid work hardening , a continuous, smooth cutting action should be maintained; thus, the machines must have a minimum of backlash and the tool and workpiece must be rigidly supported. If at all possible, avoid very small cuts and feeds.

Welding
Alloy X-750 should be welded in the stress-equalized condition, 1625°F (885°C) heat treatment, and solution treated and age hardened after welding has been completed. If this is not practical, the alloy should be welded in the solution-treated condition and age hardened after welding with or without the inclusion of a short-period stress-relieving treatment at 1625°F. Weld joints, because of softening of the alloy within the heat-affected zone, should be located where lower creep properties are required.

Typical Mechanical Properties

Room Temperature Mechanical Properties

Temper	Tensile Strength, psi	Yield Strength 0.2% offset, psi	Elongation in 2", %	Hardness, Brinell
Hot-finished + 1300°F/20 hr,A.C	170,000-206,000	120,000-163,000	25-15	313-400
Hot-finished + Annealed 1800°F/1 hr, A.C + 1350°F/ 8 hr, F.C. 100°F/hr to 1150°F (total 18 hr), A.C.	162,000-193,000	115,000-142,000	30-15	300-390
Hot-finished + 1625°F/24 hr, A.C + 1300°F/20 hr, A.C.	160,000-188,000	100,000-135,000	30-15	302-363
Cold-rolled, annealed + 1300°F/20 hr, A.C.	160,000-197,000	105,000-150,000	30-20	300-400

Bar Stock:
Treatment #1
Solution treatment 2100°F (1149°C), 2 to 4 hrs., air cool intermediate age 1550°F (843°C), 24 hrs., air cool
Final age 1300°F (704°C), 20 hrs., air cool

Test Temperature		Short-Time Tensile Properties Tests					
		Yield Strength 0.2% offset		Ultimate Tensile Strength		% Elongation in 2" (50.8 mm)	% Reduction of Area
°F	°C	ksi	MPa	ksi	MPa		
70	21.1	92	634	161	1110	22	30
1000	538.0	83	572	140	965	20	30
1200	649.0	82	565	120	827	10	21
1400	760.0	68	469	80	552	10	22
1500	816.0	45	310	47	324	20	32

Inconel X-750 - Current Inventory Stock

Special Metals INCONEL® Alloy X-750

Categories: Metal; Superalloy; Nickel Base

Material Notes: Nickel content above includes cobalt; Nb content above includes Ta. A nickel-chromium alloy similar to INCONEL alloy 600 but made precipitation hardenable by additions of aluminum and titanium. The alloy has good resistance to corrosion and oxidation along with high tensile and creep-rupture properties at temperatures to about 1300°F (700°C). Its excellent relaxation resistance is useful for high-temperature springs and bolts. Used in gas turbines, rocket engines, nuclear reactors, pressure vessels, tooling, and aircraft structures. Standard product forms are round, flats, extruded section, forging stock, plate, sheet, strip, pipe, tube, and wire.

Data provided by the manufacturer, Special Metals.

Key Words: MIL-N-7786, MIL-N-8550, MIL-S-23192, MIL-N-24114; NACE MR-01-75; AFNOR NC 15 FeT, SAE AMS 5542, 5582, 5583, 5598, 5667 - 5671, 5698, 5699, 5747, 7246, UNS N07750; BS HR505; ASTM B 637; ASME SB-637, Boiler Code Section III; Werkstoff Nr. 2.4669

Vendors: Click here to view all available suppliers for this material.

Please click here if you are a supplier and would like information on how to add your listing to this material.

Physical Properties	Metric	English	Comments
Density	8.28 g/cc	0.299 lb/in³	

Mechanical Properties	Metric	English	Comments
Tensile Strength, Ultimate	1120 MPa @Temperature 550 °C	162000 psi @Temperature 1020 °F	Precipitation Hardened prior to test
	1250 MPa	181000 psi	Precipitation Hardened. Value at room temperature.
Tensile Strength, Yield	760 MPa @Temperature 550 °C	110000 psi @Temperature 1020 °F	Precipitation Hardened prior to test; 0.2% offset
	850 MPa	123000 psi	Precipitation Hardened. Value at room temperature; 0.2% offset.
Elongation at Break	22.0 % @Temperature 550 °C	22.0 % @Temperature 1020 °F	Precipitation Hardened prior to test.
	30.0 %	30.0 %	Precipitation Hardened

Electrical Properties	Metric	English	Comments
Electrical Resistivity	0.000122 ohm-cm	0.000122 ohm-cm	
Magnetic Permeability	1.0035	1.0035	at 200 oersted (15.9 kA/m)
Curie Temperature	-125 °C	-193 °F	

Thermal Properties	Metric	English	Comments
CTE, linear 20°C	12.6 µm/m-°C	7.00 µin/in-°F	20-100°C

Specific Heat Capacity	0.431 J/g-°C	0.103 BTU/lb-°F
Thermal Conductivity	12.0 W/m-K	83.3 BTU-in/hr-ft²-°F
Melting Point	1390 - 1430 °C	2530 - 2610 °F
Solidus	1390 °C	2530 °F
Liquidus	1430 °C	2610 °F

Material Components Properties	Metric	English	Comments
Aluminum, Al	0.400 - 1.00 %	0.400 - 1.00 %	
Carbon, C	<= 0.0800 %	<= 0.0800 %	
Chromium, Cr	14.0 - 17.0 %	14.0 - 17.0 %	
Cobalt, Co	<= 1.00 %	<= 1.00 %	
Columbium (Niobium, Nb)	0.700 - 1.20 %	0.700 - 1.20 %	
Copper, Cu	<= 0.500 %	<= 0.500 %	
Iron, Fe	5.00 - 9.00 %	5.00 - 9.00 %	
Manganese, Mn	<= 1.00 %	<= 1.00 %	
Nickel, Ni	>= 70.0 %	>= 70.0 %	
Silicon, Si	<= 0.500 %	<= 0.500 %	
Sulfur, S	<= 0.0100 %	<= 0.0100 %	
Titanium, Ti	2.25 - 2.75 %	2.25 - 2.75 %	

NINC35

ATI Wah Chang
Allegheny Technologies

TECHNICAL DATA SHEET

Reactor Grade Zirconium Alloys for Nuclear Waste Disposal

ZIRCONIUM ALLOYS

Zirconium is a commercially available refractory metal with excellent corrosion resistance, good mechanical properties, very low thermal neutron cross section, and can be manufactured using standard fabrication techniques. The unique properties of zirconium made ideal cladding material for the U.S. Navy nuclear propulsion program in the 1950's. The initial commercial nuclear power reactors used stainless steel to clad the uranium dioxide fuel due to cost. But by mid-1960 zirconium alloys were the principle cladding material due to the superior neutron economy and corrosion resistance. These same zirconium alloys are available to designers of high level nuclear waste disposal containers as internal components or external cladding. Additional advantages of zirconium alloys for long term nuclear waste disposal include excellent radiation stability and 100% compatibility with existing Zircaloy fuel cladding to alleviate any concerns of galvanic corrosion.

The various zirconium alloy grades used in water-cooled nuclear reactors are also available for nuclear waste disposal components. Reactor grade designates that the material has low hafnium content suitable for nuclear service. The hafnium is typically 0.010% maximum. The American Society for Testing and Materials (ASTM) offers widely recognized grades of zirconium alloys. Zircaloy-2 (Grade R60802) is composed of Zr-1.5%Sn-0.15%Fe-0.1%Cr-0.05%Ni and has been predominantly used as fuel cladding in Boiling Water Reactors (BWR) and as calandria tubing in CANadian Deuterium Uranium (CANDU) reactor types. Zircaloy-4 (Grade R60804) has removed the nickel and increased the iron content for less hydrogen uptake in certain reactor conditions. The alloy is typically used as fuel cladding in Pressurized Water Reactors (PWR) and CANDU reactors. The nominal Zircaloy-4 composition is Zr-1.5%Sn-0.2%Fe-0.1%Cr. Refinements in the ingot homogeneity have allowed tighter control of the alloy elements within the ASTM specification. Controlled Composition Zircaloy offers optimized in-reactor corrosion resistance by adjusting the alloy aim point within the ASTM specification ranges. Controlled Composition Zircaloy-4 has lower tin (1.3%) and higher iron (0.22%) than the standard grade. Zr-2.5Nb (Grade R60904) is a binary alloy with niobium to increase the strength. The alloy has been utilized for pressure tubes in CANDU reactors. Non-reactor grade Zirconium 702 (Grade R60702) has 4.5% maximum hafnium and is also available from Wah Chang.

Zirconium alloys have superior thermal properties compared to other traditional materials in consideration for spent nuclear fuel containers. Zirconium alloys have a thermal conductivity more than 30% higher than stainless steel alloys. The linear coefficient of thermal expansion for Zirconium alloys is nearly one-third the value for stainless steel giving zirconium alloys superior dimensional stability at elevated temperatures. This is an advantage in nuclear waste containers where temperatures could exceed 200°C for hundreds of years.

Zircaloy-2 and Zircaloy-4 have a hexagonal close-packed (HCP) crystal structure at room temperature as an alpha phase. The beta phase is body centered cubic (BCC) and begins to form upon heating to approximately 810°C. The fraction of beta phase increases with temperature until complete transformation to beta phase

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Custserv@wahchang.com • www.alleghenytechnologies.com/wahchang

occurs at approximately 980°C. Zircaloy exhibits anisotropy as a result of the HCP crystal structure. The hexagonal crystal deforms by both slip and twinning to produce a strong preferred orientation of the crystals (texture) during cold working. Typically, cold rolled Zircaloy strip will have a strong normal texture where most of the basal poles of the hexagonal crystals are orientated about 35 degrees to the transverse plane of the strip. The anisotropic properties of Zircaloy strip results in significantly higher yield strength values in the transverse direction. The control of crystallographic orientation allows designers to optimize material properties.

ZIRCONIUM ALLOY PROPERTIES

Zirconium resists corrosive attack in most organic and mineral acids, strong alkalis, and some molten salts. Solutions of nitric acid (HNO_3), sulfuric acid (H_2SO_4), and hydrochloric acid (HCl) with impurities of ferric, cupric and nitrate ions generally result in corrosion rates of less than 0.13 mm/a (5 mpy) even at temperatures well above the boiling point curve. A tightly adherent and protective oxide film protects the metal-oxide interface to provide corrosion resistance. An additional benefit for zirconium alloys in long-term geological disposal options is the inert nature of zirconium oxide. Application of zirconium alloys alleviates the concern of nickel and chromium contamination in the ground water in severely corroded spent fuel containers.

Zirconium alloys produced by Wah Chang are available in a wide variety of sizes and shapes including plate, strip, sheet, foil, tubular products, rod, and wire. Wrought products are typically supplied in an annealed and conditioned form. One of our specialties at Wah Chang is the ability to develop alloys to meet your specifications. If you have an unusual alloy or size requirement, call us and we will be happy to help in the developmental process.

THERMAL NEUTRON CROSS SECTIONS (BARNS)

Magnesium	0.059
Lead	0.17
Zirconium	0.18
Zircaloy-4	0.22
Aluminum	0.23
Iron	2.56
Austenitic Stainless Steel	3.1
Nickel	4.5
Titanium	6.1
Hafnium	104
Boron	750
Cadmium	2,520
Gadolinium	48,890

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COMPOSITION (WEIGHT PERCENT)

Name	Zircaloy-2	Zircaloy-4	Zr-2.5Nb
UNS Grade	R60802	R60804	R60904
Tin	1.20-1.70	1.20-1.70	---
Iron	0.07-0.20	0.18-0.24	---
Chromium	0.05-0.15	0.07-0.13	---
Nickel	0.03-0.08	---	---
Niobium	---	---	2.40-2.80
Oxygen	Per P.O.	Per P.O.	Per P.O.
Iron + Chromium + Nickel	0.18-0.38	---	---
Iron + Chromium	---	0.28-0.37	---

MAXIMUM IMPURITIES, WEIGHT %

Name	Zircaloy-2	Zircaloy-4	Zr-2.5Nb
Aluminum	0.0075	0.0075	0.0075
Boron	0.00005	0.00005	0.00005
Cadmium	0.00005	0.00005	0.00005
Carbon	0.027	0.027	0.027
Chromium	---	---	0.010
Cobalt	0.0020	0.0020	0.0020
Copper	0.0050	0.0050	0.0050
Hafnium	0.010	0.010	0.005
Hydrogen	0.0025	0.0025	0.0010
Iron	---	---	0.150
Magnesium	0.0020	0.0020	0.0020
Manganese	0.0050	0.0050	0.0050
Molybdenum	0.0050	0.0050	0.0050
Nickel	---	0.0070	0.0070
Nitrogen	0.0080	0.0080	0.0065
Phosphorus	---	---	0.0020
Silicon	0.0120	0.0120	0.010
Tin	---	---	0.0050
Tungsten	0.010	0.010	0.005
Titanium	0.0050	0.0050	0.0050
Uranium (total)	0.00035	0.00035	0.00035

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PROPERTIES OF ZIRCALOY-4

Density	6.55 g/cc (0.237 lbs/cu.-in.)
Coefficient of Thermal Expansion at 25°C	6 µm/m °C (3.3 µin/in-°F)
Heat Capacity	0.285 J/g-°C (0.07 BTU/lb-°C)
Thermal Conductivity	21.5 Watts/m-K (149 BTU-in/hr-ft^2 -°F)
Melting Point	1850°C (3,362°F)
Alpha→Alpha + Beta Phase Transformation	~810°C
Alpha + Beta→Beta Phase Transformation	~980°C
Hardness	89 Rb average
Modulus of Elasticity	99.3 Gpa (14,402 ksi)
Poisson's Ratio	0.37
Shear Modulus	36.2 Gpa (5,249 ksi)

MECHANICAL PROPERTIES OF ZIRCALOY-4 ANNEALED 2 MM THICK STRIP

Orientation	Longitudinal		Transverse	
Test Temperature	Room Temp.	288°C	Room Temp.	288°C
Ultimate Tensile Strength,				
MPa	541	271	515	241
(ksi)	(78.4)	(39.3)	(74.6)	(34.9)
Yield Strength,				
MPa	80	152	468	170
(ksi)	(55.2)	(22.0)	(67.8)	(25.6)
Elongation, %	28	43	29	44

CORROSION RATE DATA FOR ZIRCALOY-4

Corrosive Media	Concentration %	Temperature °C	Corrosion Rate mm/a (MPY)
HCl	70	160	0.36 (14)
HNO_3	70	120	0.05 (2)
H_2SO_4	70	150	<0.13 (<5)
$CuCl_2$	0.1	144	0.03 (1)
$FeCl_3$	1	135	0.18 (7)
NaCl	25	250	nil

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ATTACHMENT 5

Nickel Calculation

Assumptions

1.) Nickel has the highest weight % in Inconel X-750 (70%)
2.) Calculation performed similar to Chromium & Cadmium.
3.) Dissolved metal has concentration as original material

- Avg waste weight 600 kg [42 drums / tare weight 27 kg (55 gal)]
- Max possible dissolved Nickel = Total mass dissolved 1442.2 g × 70% = 1010 g
- Nickel/drum = 1010 g / 42 = 24 g
- Nickel content in waste = 24 g / 297,600 g
  = 8.06 E-5 g/g
  = 80.6 ppm

If TCLP extract is included (100 g sample / 2000 ml extraction fluid)

Nickel in Sample = 100 × 8.06 E-5 g = 8.06 E-3 g

Assume a density of 1 ml/g for the extract and assuming all Nickel leache (this is conservative)

Nickel concentration in extract = 8.06 E-3 g / 2000 = 4.02 E-6 g Ni/g extract
= 4.02 E-6 g × 1000000
= 4.02 ppm

* Avg drum weight 600 kg
  52% lead shielding (Not included = 322.4 kg = 322,400 g
  48% Cemented waste (cement/steel) = 297.6 kg = 297,600 g

Kiel Lakel
9-14-11